Supporting Information for

Enantioselective synthesis of cyclic α-aminoboronates via copper-catalyzed dearomative borylation of 4-quinolinols

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1. General information

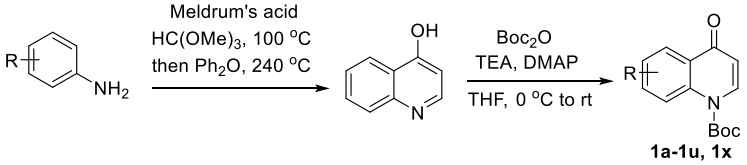
General. Unless otherwise noted, all reactions were carried out in a flame-dried schlenk tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Visualization was accomplished by exposure to a UV lamp, and/or treatment with a solution of $KMnO_4$ or a solution of Phosphomolybdic Acid (PMA) followed by brief heating with a heating gun. Column chromatography was undertaken on silica gel (200-300 mesh). The ***deactivated silica gel*** (35 wt% H_2O) was prepared by mixing silica gel and deionized water (65:35 by weight), followed by vigorous shaking until the mixture turned to a fluffy powder then it was allowed to use.

Structural analysis. NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents ($CDCl_3$) and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 101 MHz (signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation), Chemical shift were reported in ppm on the δ scale relative to $CHCl_3$ (δ = 7.26 for ^{1}H NMR, δ = 77.00 for ^{13}C NMR). ^{11}B NMR spectra at 128 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. ^{19}F NMR spectra were recorded on Bruker Avance-400 spectrometer (375 MHz). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). High resolution mass Spectra (HRMS) were obtained on a Bruker Apex IV FTMS spectrometer or an Agilent 6224 LC/MS TOF spectrometer. Optical rotations were obtained on Anton-paar polarimeter; concentration (c) is in g/100 mL. Melting points are reported with a Hanon MP300 or Shanghai YiCe WRX-4 apparatus. Enantiomeric excesses (ee) were determined by chiral HPLC analysis using Waters 2489 and Agilent 1260. Series chromatographs using a mixture of HPLC-grade hexane and isopropanol as eluent.

Materials. Commercial reagents were purchased from Adamas, J&K, Acros Organics, Energy, Sigma-Aldrich, Alfa Aesar, or TCI and used as received unless otherwise noted. THF were purified by distillation over sodium/benzophenone and stored under argon. All air-sensitive manipulations were carried out under an argon atmosphere in a glovebox or by standard Schlenk techniques.

2. Synthesis of starting materials 1a-1x

2.1 General procedures for the synthesis of starting materials 1a-1u, 1x



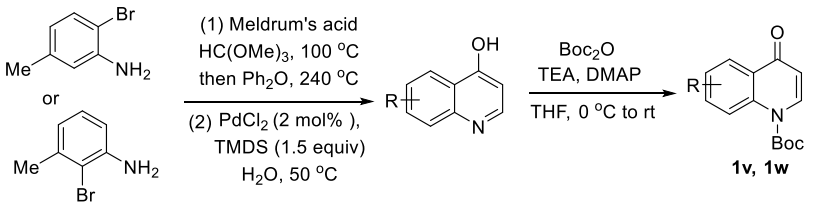
The preparation of 4-quinolinols and *N*-Boc protected 4-quinolones was according to literature procedures.[1,2] A solution of Meldrum's acid (3.24 g, 22.5 mmol) and trimethyl orthoformate (40 mL) was heated to reflux at 110 ºC for 2 h under nitrogen. The aniline (15 mmol) was added to the solution carefully and the mixture was heated to reflux at 100 ºC for 2 h. The solvent was evaporated in vacuo to give the crude product, which was washed with methanol (20 mL) to give pure products. Then diphenyl ether (30 mL) were heated to 240 ºC (internal temperature), the products were added carefully within 10 minutes and stirred at this temperature for 5 minutes. The solution was allowed to cool to room temperature and hexane (20 mL) was added. The precipitate formed was collected by filtration, washed with hexane and dichloromethane (30 mL), and dried in vacuo, the crude product was directly used for next step.

Triethylamine (0.63 mL, 4.5 mmol, 1.5 eq), di-*tert*-butyl dicarbonate (1.03 mL, 4.5 mmol, 1.5 eq), and dimethylaminopyridine (catalytic amount) were added to a cooled and stirred suspension 4(H)-quinolones (3 mmol) in anhydrous tetrahydrofuran (20 mL). The reaction was stirred at room temperature for 2 h. The mixture was concentrated, and the residue was solubilized with ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulfate. The organic solvent was evaporated, and the crude product was purified by column chromatography.

[1] W. Zhang, Z. Li, M. Zhou, F. Wu, X. Hou, H. Luo, H. Liu, X. Han, G. Yan, Z. Ding, R. Li, *Bioorg. Med. Chem. Lett*., 2014, **24**, 799.

[2] F. Rosi, G. C. Crucitti, A. Iacovo, G. Miele, L. Pescatori, R. Di Santo and R. Costi, *Syn. Commun*., 2013, **43**, 1063.

2.2 General procedures for the synthesis of starting materials 1v, 1w



A solution of Meldrum's acid (3.24 g, 22.5 mmol) and trimethyl orthoformate (40 mL) was heated to reflux at 110 °C for 2 h under nitrogen. The aniline (15 mmol) was added to the solution carefully and the mixture was heated to reflux at 100 °C for 2 h. The solvent was evaporated in vacuo to give the crude product, which was washed with methanol (20 mL) to give pure products. Then diphenyl ether (30 mL) were heated to 240 °C (internal temperature), the products were added carefully within 10 minutes and stirred at this temperature for 5 minutes. The solution was allowed to cool to room temperature and hexane (20 mL) was added. The precipitate formed was collected by filtration, washed with hexane and dichloromethane (30 mL), and dried *in vacuo*, the crude product was directly used for next step.

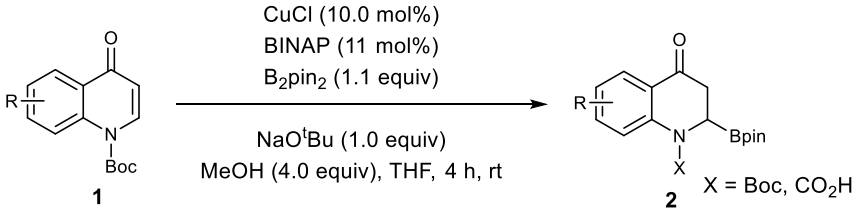
Dehalogenation catalyzed by $PdCl_2$ was according to literature procedures.[3] To a sample vial equipped with a Teflon-coated magnetic stir bar were added in sequence $PdCl_2$ (2%), bromide substituted 4-quinolinols (3 mmol) and deionized water (15 mL). The vial was covered with a phenolic cap and the contents were stirred on a reaction block at 50 °C. After two min, to the resultant suspension was added 1,1,3,3-tetramethyldisiloxane (TMDS) (0.375 mmol), dropwise. (Caution! The TMDS should be added slowly, and the addition should be paused if a vigorous generation of dihydrogen is observed). The vial was again covered and the contents stirred until complete consumption of the starting material. The resulting mixture was extracted with EtOAc passed through a short pad of Celite. The organic extracts were concentrated *in vacuo*, then the crude product was directly used for next step.

Triethylamine (0.63 mL, 4.5 mmol, 1.5 eq), di-*tert*-butyl dicarbonate (1.03 mL, 4.5 mmol, 1.5 eq), and dimethylaminopyridine (catalytic amount) were added to a cooled and stirred suspension 4(H)-quinolones (3 mmol) in anhydrous tetrahydrofuran (20 mL). The reaction was stirred at room temperature for 2 h. The mixture was concentrated, and the residue was solubilized with ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulfate. The organic solvent was evaporated, and the crude product was purified by column chromatography.

[3] A. Bhattacharjya, P. Klumphu and B. H. Lipshutz, *Org. Lett.,* 2015, **17**, 1122.

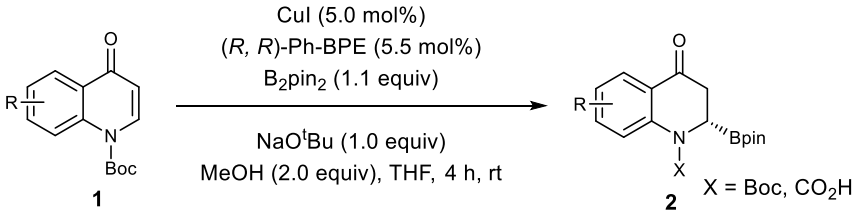
3. General procedures for the synthesis of α-aminoboronates 2a-2x

3.1 General procedures for the synthesis of racemic α-aminoboronates 2a-2x



The reported method for the synthesis of racemic α-aminoboronates were slightly modified.[4] In an argon-filled glovebox, to a 10-mL flame-dried Schlenk tube charged with CuCl (1.98 mg, 0.02 mmol), BINAP (13.70 mg, 0.022 mmol), B_2pin_2 (55.86 mg, 0.22 mmol) and NaO^{t}Bu (19.22 mg, 0.2 mmol) was added THF (0.5 mL). The resulting mixture was allowed to stir at room temperature for 0.5 h. A solution of **1** (0.2 mmol) in THF (0.5 mL) was added followed by methanol (32.4 μL, 0.8 mmol) and the reaction was allowed to stir at room temperature for 4 h. After removal of the solvent, the residue was dissolved in dichloromethane (5 mL), then the organic layer was washed with aqueous NaCl solution and dried over anhydrous sodium sulfate. The organic solvent was evaporated, and the crude product was purified by column chromatography on deactivated silica gel using eluent mixtures of hexane and ethyl acetate or dichloromethane and methanol to afford corresponding racemic α-aminoboronates **2**.

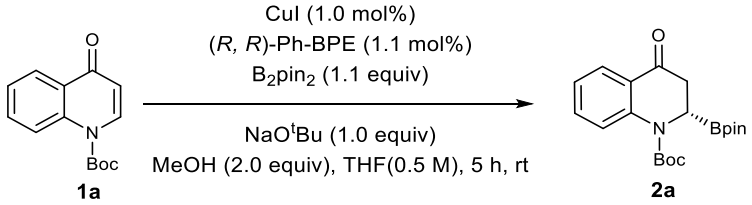
3.2 General procedures for the synthesis of chiral α-aminoboronates 2a-2x



In an argon-filled glovebox, to a 10-mL flame-dried Schlenk tube charged with CuI (1.90 mg, 0.01 mmol), (*R, R*)-Ph-BPE (5.57 mg, 0.011 mmol), B_2pin_2 (55.86 mg, 0.22 mmol) and NaO^{t}Bu (19.22 mg, 0.2 mmol) was added THF (0.5 mL). The resulting mixture was allowed to stir at room temperature for 0.5 h. A solution of **1** (0.2 mmol) in THF (0.5 mL) was added followed by methanol (16.2 μL, 0.4 mmol) and the reaction was allowed to stir at room temperature for 4 h. After removal of the solvent, the residue was dissolved in dichloromethane (5 mL), then the organic layer was washed with aqueous NaCl solution and dried over anhydrous sodium sulfate. The organic solvent was evaporated, and the crude product was purified by column chromatography on deactivated silica gel using eluent mixtures of hexane and ethyl acetate or dichloromethane and methanol to afford corresponding chiral α-aminoboronates **2**.

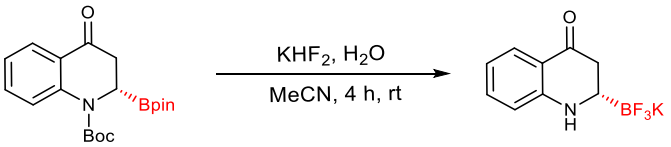
[4] X. Feng, J. Yun, *Chem. Commun.* **2009**, 6577–6579.

4. Gram-scale dearomative borylation of 1a



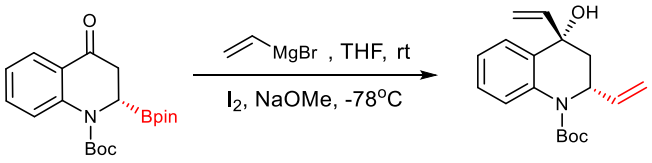
In an argon-filled glovebox, to a 100-mL flame-dried Schlenk tube charged with CuI (9.5 mg, 0.05 mmol), (*R, R*)-Ph-BPE (27.86 mg, 0.055 mmol), B_2pin_2 (1396 mg, 5.5 mmol) and NaO^{t}Bu (480 mg, 5 mmol) was added THF (5 mL). The resulting mixture was allowed to stir at room temperature for 0.5 h. A solution of **1a** (1226 mg, 5 mmol) in THF (5 mL) was added followed by methanol (0.4 mL, 10 mmol) and the reaction was allowed to stir at room temperature for 5 h. After removal of the solvent, the residue was dissolved in dichloromethane (30 mL), then the organic layer was washed with aqueous NaCl solution and dried over anhydrous sodium sulfate. The organic solvent was evaporated, and the crude product was purified by column chromatography on deactivated silica gel using PE/EtOAc (6:1) as the eluent to affording corresponding chiral α-aminoboronate **2a** (1.27 g, 67% yield). The enantioselective excess of the product was determined to be >99% ee by chiral HPLC.

5. Synthetic transformation of the products



2a, >99% ee **3a**, 86%

The reaction was conducted according to a reported procedure.[5] Solid KHF_2 (117 mg, 1.5 mmol) was added to a solution of boronate ester **2a** (93.31 mg, 0.25 mmol) in acetonitrile (2 mL) at 0 ºC. Water (2 mL) was added to the stirred suspension at 0 ºC. The mixture was warmed to room temperature then stirred for 3 h. The solvent was evaporated, hot acetone was added, Removed the inorganic salts by filtration, the filtrate was dilute with hexane, then stored at fridge overnight. The resulting solid was collected after filtration and dissolved in water then remove water on vacuum. Then afforded product **3a** in 86% yield.



2a, >99% ee **3b**, 52%

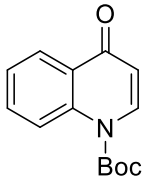
The reaction was carried out using the Aggarwal[6] protocol as follows: To a solution of boronate ester **2a** (0.25 mmol) in anhydrous THF (2.0 mL) at room temperature was added a vinylmagnesium bromide (1.0 M in THF, 1.0 mmol) dropwise. The resulting mixture was stirred at room temperature for 30 min and cooled down to –78 °C. A solution of iodine (1.0 mmol) in MeOH (2 mL) was added dropwise to the reaction mixture via cannula, followed 30 min later by a solution of NaOMe (2.0 mmol) in MeOH (3 mL). The reaction mixture was then allowed to warm to room temperature and stirred for an additional 1 h, diluted with pentane (20 mL) and washed with a 20% aq. $Na_2S_2O_3$ solution and water. The phases were separated, the aqueous layer was extracted with pentane (2 × 10 mL), the combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was purified by flash column chromatography to obtain the desired product **3b** in 52% yield.

[5] Y. J. Zuo, Z. Zhong, Y. Fan, X. Li, X. Chen, Y. Chang, R. Song, X. Fu, A. Zhang and C. M. Zhong, *Org. Biomol. Chem*. 2018, **16**, 9237.

[6] R. P. Sonawane, V. Jheengut, C. Rabalakos, R. Larouche-Gauthier, H. K. Scott and V. K. Aggarwal, *Angew. Chem., Int. Ed*. 2011, **50**, 3760.

6. Characterization data of 1a-2x and 3a-3b

Compound 1a (CAS:1421590-61-5)

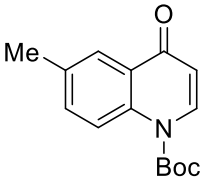


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.9 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.61 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.5 Hz, 1H), 1.64 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.96, 149.87, 138.72, 138.56, 132.54, 126.58, 126.42, 125.11, 119.96, 111.83, 86.55, 27.94.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 4:1). White solid, isolated yield: 82%. Spectral data matched those reported in the literature.[2]

Compound 1b (CAS:2416334-02-4)

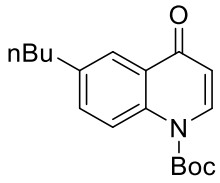


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.9 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.20 – 8.13 (m, 1H), 7.47 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.24 (d, *J* = 8.5 Hz, 1H), 2.45 (s, 3H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.17, 149.94, 138.49, 136.54, 135.11, 133.87, 126.47, 125.96, 119.89, 111.71, 86.38, 27.98, 20.76.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 4:1). White solid, isolated yield: 89%. Spectral data matched those reported in the literature.[7]

Compound 1c



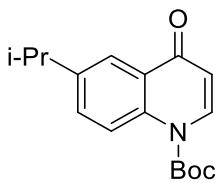
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 9.0 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 2.3 Hz, 1H), 7.48 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.24 (d, *J* = 8.5 Hz, 1H), 2.76 – 2.67 (m, 2H), 1.68 (s, 9H), 1.66 – 1.60 (m, 2H), 1.40 – 1.31 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.20, 149.94, 140.04, 138.46, 136.66, 133.24, 126.49, 125.33, 119.90, 111.68, 86.36, 34.86, 33.33, 27.96, 22.25, 13.90.

HRMS (ESI^+, m/z): calcd for $C_{18}H_{24}NO_3$ ($[M+H]^+$): 302.1750, found: 302.1744.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 85-86 ºC, isolated yield: 70%.

Compound 1d



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 9.0 Hz, 1H), 8.27 (m, 2H), 7.55 (dd, *J* = 8.9, 1.5 Hz, 1H), 6.25 (d, *J* = 8.4 Hz, 1H), 3.04 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.68 (s, 9H), 1.31 (d, *J* = 6.9 Hz, 6H).

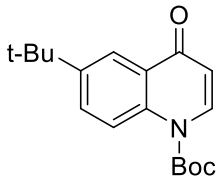
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.28, 149.97, 145.93, 138.46, 136.75, 131.48, 126.56, 123.34, 120.03, 111.69, 86.39, 33.59, 27.97, 23.79.

HRMS (ESI^+, m/z): calcd for $C_{17}H_{23}NO_3$ ($[M+H]^+$): 288.1594, found: 288.1592.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 4:1). White solid, mp = 47-48 ºC, isolated yield: 86%.

[7] B. He, P. Phansavath and V. Ratovelomanana-Vidal, *Org. Chem. Front*. 2020, **7**, 975.

Compound 1e



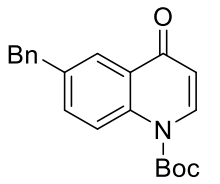
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.1 Hz, 1H), 8.33 (m, 2H), 7.72 (d, *J* = 9.0 Hz, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 1.68 (s, 9H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.31, 149.96, 148.23, 138.40, 136.47, 130.44, 126.22, 122.25, 119.80, 111.73, 86.37, 34.65, 31.18, 27.96.

HRMS (ESI$^+$, m/z): calcd for $C_{18}H_{24}NO_3$ ([M+H]$^+$): 302.1750, found: 302.1751.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 4:1). White solid, mp = 76-77 ºC, isolated yield: 83%.

Compound 1f



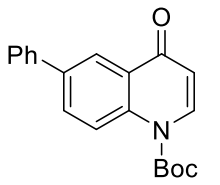
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 9.0 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 1.7 Hz, 1H), 7.44 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.24 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 3H), 6.23 (d, *J* = 8.5 Hz, 1H), 4.04 (s, 2H), 1.64 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.04, 149.84, 140.38, 138.68, 138.35, 137.00, 133.54, 128.88, 128.58, 126.55, 126.30, 125.94, 120.34, 111.71, 86.55, 41.27, 27.92.

HRMS (ESI$^+$, m/z): calcd for $C_{21}H_{22}NO_3$ ([M+H]$^+$): 336.1594, found: 336.1598.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 4:1). White solid, mp = 77-78 ºC, isolated yield: 78%.

Compound 1g



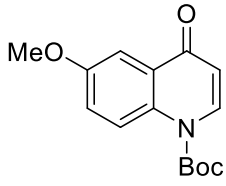
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 9.1 Hz, 1H), 8.62 (d, *J* = 2.4 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 7.91 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.50 – 7.43 (m, 2H), 7.40 – 7.34 (m, 1H), 6.28 (d, *J* = 8.5 Hz, 1H), 1.69 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.08, 149.87, 139.20, 138.65, 137.79, 137.77, 131.21, 128.93, 127.81, 127.11, 126.89, 124.19, 120.65, 111.95, 86.68, 27.99.

HRMS (ESI$^+$, m/z): calcd for $C_{20}H_{20}NO_3$ ([M+H]$^+$): 322.1437, found: 322.1441.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 122-123 ºC, isolated yield: 81%.

Compound 1h (CAS: 2416334-03-5)

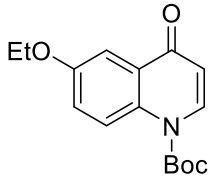


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.6 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 2.9 Hz, 1H), 7.23 (dd, *J* = 9.5, 3.0 Hz, 1H), 6.23 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.56, 156.69, 149.79, 138.13, 132.76, 127.87, 122.20, 121.73, 110.92, 105.87, 86.38, 55.58, 27.89.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, isolated yield: 78%. Spectral data matched those reported in the literature.[9]

Compound 1i



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 9.6 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 3.2 Hz, 1H), 7.24 (dd, *J* = 9.6, 3.2 Hz, 1H), 6.23 (d, *J* = 8.4 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 1.67 (s, 9H), 1.45 (t, *J* = 7.0 Hz, 3H).

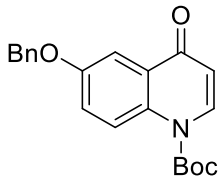
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.74, 156.17, 149.89, 138.09, 132.73, 127.95, 122.67, 121.74, 111.01, 106.61, 86.39, 63.90, 27.96, 14.69.

HRMS (ESI$^+$, m/z): calcd for $C_{16}H_{20}NO_4$ ([M+H]$^+$): 290.1386, found: 290.1384.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid,

mp = 123-124 ºC, isolated yield: 84%.

Compound 1j



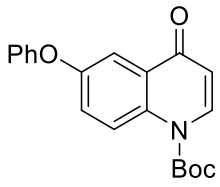
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 9.6 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 3.2 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 6.24 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H), 1.67 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.68, 155.97, 149.88, 138.19, 136.42, 133.03, 128.63, 128.15, 127.97, 127.71, 122.82, 121.90, 111.10, 107.18, 86.48, 70.32, 27.98.

HRMS (ESI$^+$, m/z): calcd for $C_{21}H_{22}NO_4$ ([M+H]$^+$): 352.1543, found: 352.1544.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 3:1). White solid, mp = 96-97 ºC, isolated yield: 81%.

Compound 1k



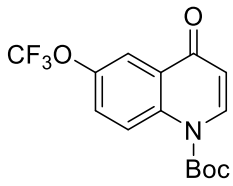
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 9.5 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 2.9 Hz, 1H), 7.37 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.22 (d, *J* = 8.5 Hz, 1H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.44, 156.49, 154.73, 149.85, 138.50, 134.26, 130.00, 128.23, 124.13, 123.98, 122.21, 119.30, 113.63, 111.26, 86.67, 27.98.

HRMS (ESI$^+$, m/z): calcd for $C_{20}H_{20}NO_4$ ([M+H]$^+$): 338.1386, found: 338.1385.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 91-92 ºC, isolated yield: 65%.

Compound 1l



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 9.6 Hz, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.27 – 8.14 (m, 1H), 7.49 (dd, *J* = 9.7, 3.1 Hz, 1H), 6.27 (d, *J* = 8.5 Hz, 1H), 1.69 (s, 9H).

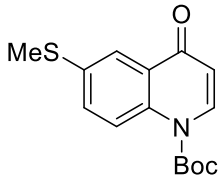
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.87, 149.57, 146.14 (q, *J* = 2.0 Hz), 139.01, 136.82, 127.97, 125.42, 122.44, 121.72, 119.15, 117.60, 111.68, 87.22, 27.91.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.98.

HRMS (ESI$^+$, m/z): calcd for $C_{15}H_{15}F_3NO_4$ ([M+H]$^+$): 330.0947, found: 330.0949.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 124-125 ºC, isolated yield: 85%.

Compound 1m



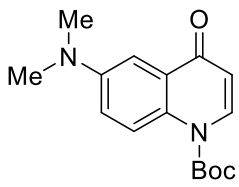
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 9.2 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 2.2 Hz, 1H), 7.51 (dd, *J* = 9.2, 2.3 Hz, 1H), 6.26 (d, *J* = 8.5 Hz, 1H), 2.57 (s, 3H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.33, 149.74, 138.50, 136.41, 135.95, 131.04, 127.07, 121.84, 120.51, 111.84, 86.70, 27.96, 15.47.

HRMS (ESI$^+$, m/z): calcd for $C_{15}H_{19}NO_3S$ ([M+H]$^+$): 292.1001, found: 292.1005.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 129-130 ºC, isolated yield: 81%.

Compound 1n



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 9.5 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.10 (m, 1H), 6.20 (d, *J* = 8.3 Hz, 1H), 3.04 (s, 6H), 1.67 (s, 9H).

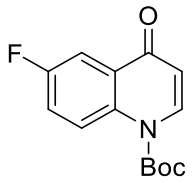
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.26, 150.05, 147.74, 137.65, 129.77, 127.66,

121.11, 118.40, 110.63, 106.15, 85.95, 40.52, 28.00.

HRMS (ESI$^+$, m/z): calcd for $C_{16}H_{21}N_2O_3$ ([M+H]$^+$): 289.1546, found: 289.1549.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 4:1). Yellow solid, mp = 109-110 °C, isolated yield: 77%.

Compound 1o (CAS: 2416334-10-4)



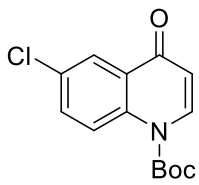
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 9.6, 4.5 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 8.00 (dd, *J* = 8.7, 3.2 Hz, 1H), 7.38 (ddd, *J* = 10.2, 7.4, 3.2 Hz, 1H), 6.24 (d, *J* = 8.5 Hz, 1H), 1.69 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.10 (d, *J* = 2.0 Hz), 159.62 (d, *J* = 249.4 Hz), 149.69, 138.85, 134.94 (d, *J* = 2.0 Hz), 134.93, 128.52 (d, *J* = 6.0 Hz), 122.70 (d, *J* = 7.0 Hz), 120.63 (d, *J* = 24.2 Hz), 111.32 (d, *J* = 22.2 Hz), 86.94, 27.94.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.55.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, isolated yield: 84%. Spectral data matched those reported in the literature.[7]

Compound 1p (CAS: 2416334-08-0)

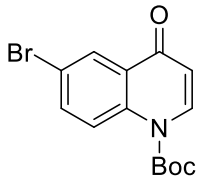


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 9.4 Hz, 1H), 8.30 (dd, *J* = 7.2, 5.8 Hz, 2H), 7.56 (dd, *J* = 9.3, 2.4 Hz, 1H), 6.23 (d, *J* = 8.5 Hz, 1H), 1.69 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.62, 149.51, 138.88, 136.91, 132.56, 131.25, 127.74, 125.72, 121.94, 111.83, 87.08, 27.91.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, isolated yield: 80%. Spectral data matched those reported in the literature.[7]

Compound 1q (CAS: 2416334-07-9)

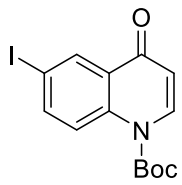


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 9.4 Hz, 1H), 8.46 (d, *J* = 2.3 Hz, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 9.3, 2.3 Hz, 1H), 6.25 (d, *J* = 8.5 Hz, 1H), 1.69 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.54, 149.51, 138.90, 137.37, 135.38, 128.98, 128.01, 122.09, 119.07, 111.97, 87.11, 27.94.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, isolated yield: 89%. Spectral data matched those reported in the literature.[7]

Compound 1r (CAS: 2416334-06-8)

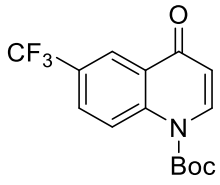


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.8 Hz, 1H), 8.37 (d, *J* = 9.3 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 9.2, 1.8 Hz, 1H), 6.25 (d, *J* = 8.5 Hz, 1H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.42, 149.50, 141.02, 138.90, 138.03, 135.31, 128.11, 122.07, 112.11, 89.92, 87.11, 27.96.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, isolated yield: 70%. Spectral data matched those reported in the literature.[7]

Compound 1s (CAS: 2416334-11-5)



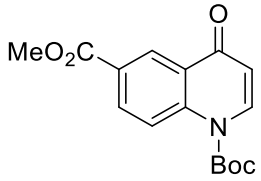
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 9.2 Hz, 1H), 8.66 (d, *J* = 2.3 Hz, 1H), 8.35 (d, *J* = 8.6 Hz, 1H), 7.85 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.31 (d, *J* = 8.6 Hz, 1H), 1.70 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.97, 149.48, 140.54, 139.27, 128.69 (q, *J* = 4.0 Hz), 127.28 (q, *J* = 34.3 Hz), 126.39, 124.30 (q, *J* = 4.0 Hz), 123.60 (q, *J* = 273.7 Hz), 121.07, 112.42, 87.50, 27.91.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, isolated yield: 90%. Spectral data matched those reported in the literature.[7]

Compound 1t



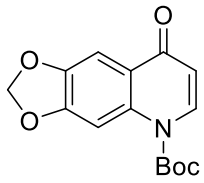
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.66 (d, *J* = 9.1 Hz, 1H), 8.33 – 8.27 (m, 2H), 6.30 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H), 1.70 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.46, 166.00, 149.59, 141.39, 139.05, 132.92, 128.67, 126.82, 126.27, 120.30, 112.50, 87.28, 52.31, 27.94.

HRMS (ESI^+, m/z): calcd for $C_{16}H_{18}NO_5$ ($[M+H]^+$): 304.1179, found: 304.1181.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 243-244 °C, isolated yield: 79%.

Compound 1u



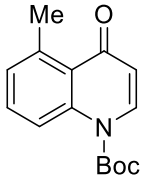
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 7.69 (s, 1H), 6.18 (d, *J* = 8.4 Hz, 1H), 6.08 (s, 2H), 1.67 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.75, 152.05, 149.87, 145.85, 137.66, 135.27, 122.67, 111.23, 103.57, 102.15, 100.00, 86.67, 27.90.

HRMS (ESI^+, m/z): calcd for $C_{15}H_{16}NO_5$ ($[M+H]^+$): 290.1023, found: 260.1025.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 4:1). White solid, mp = 131-132 °C, isolated yield: 72%.

Compound 1v



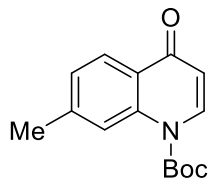
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.46 (m, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.15 (d, *J* = 8.4 Hz, 1H), 2.88 (s, 3H), 1.66 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.42, 150.31, 141.03, 140.13, 137.02, 131.16, 128.41, 125.36, 118.16, 113.59, 86.13, 27.96, 24.02.

HRMS (ESI^+, m/z): calcd for $C_{15}H_{18}NO_3$ ($[M+H]^+$): 260.1281, found: 260.1285.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 77-78 °C, isolated yield: 68%.

Compound 1w



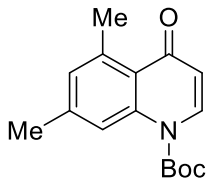
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.19 (dd, *J* = 8.2, 4.6 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.14 (d, *J* = 8.5 Hz, 1H), 2.42 (s, 3H), 1.61 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.98, 149.97, 143.50, 138.69, 138.52, 126.60, 126.38, 124.52, 119.83, 111.81, 86.39, 27.98, 22.34.

HRMS (ESI^+, m/z): calcd for $C_{15}H_{18}NO_3$ ($[M+H]^+$): 260.1281, found: 260.1285.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 109-110 °C, isolated yield: 67%.

Compound 1x



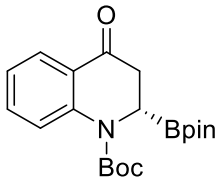
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.1, 4.3 Hz, 2H), 6.93 (d, *J* = 4.5 Hz, 1H), 6.07 (m, 1H), 2.82 (s, 3H), 2.39 (s, 3H), 1.65 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.06, 150.25, 141.64, 140.56, 140.13, 136.76, 129.69, 123.10, 118.10, 113.41, 85.88, 27.88, 23.88, 21.94.

HRMS (ESI^+, m/z): calcd for $C_{16}H_{20}NO_3$ ($[M+H]^+$): 274.1437, found: 274.1440.

Purification by flash column chromatography on silica gel (eluent, hexane: EtOAc = 5:1). White solid, mp = 67-68 °C, isolated yield: 88%

Compound 2a



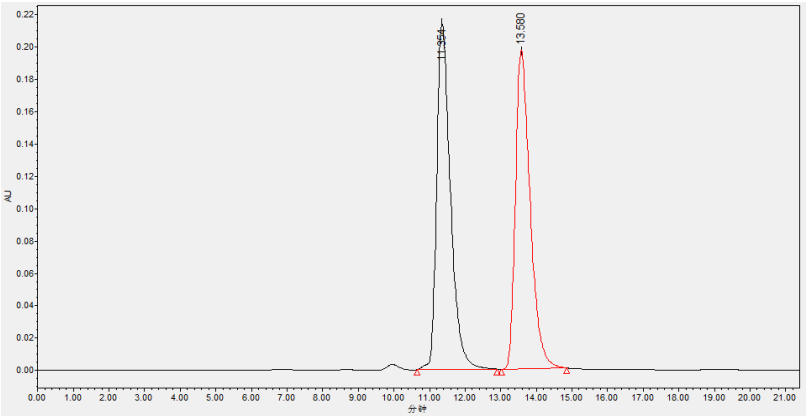
White solid, 82% yield, >99% ee, mp = 120-121 °C, α_D^{25}= -62 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.23 – 7.16 (m, 1H), 3.43 (dd, *J* = 15.0, 3.5 Hz, 1H), 2.93 (dd, *J* = 17.8, 15.0 Hz, 1H), 2.68 (dd, *J* = 17.8, 3.6 Hz, 1H), 1.64 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.10, 159.11, 140.36, 134.12, 128.06, 124.86, 124.51, 120.52, 89.90, 80.95, 40.05, 28.42, 25.12, 24.73.

^{11}B NMR (128 MHz, $CDCl_3$) δ 15.57.

HRMS (ESI$^+$, m/z): calcd for $C_{20}H_{29}BNO_5$ ([M+H]$^+$): 374.2133, found: 374.2130.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min):11.22 (major) and 13.48 (minor).



Peak ID	Ret. time	Height	Area	Area%
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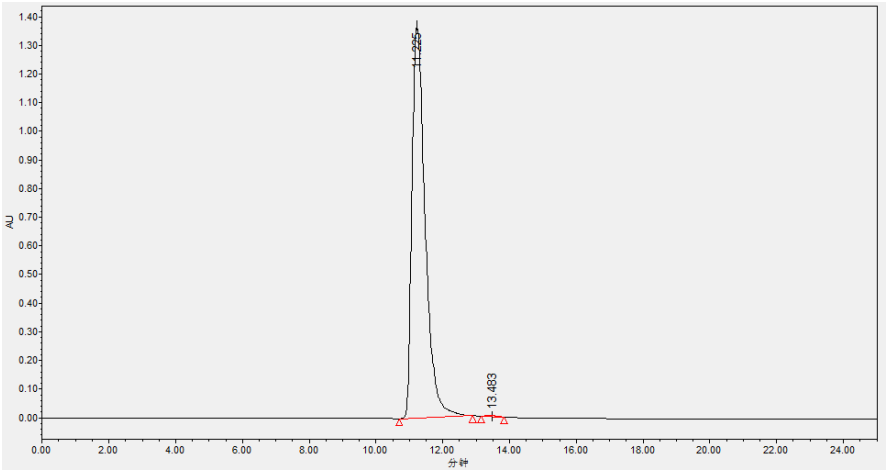
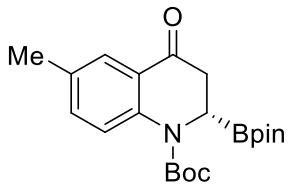
2	13.580	196969	5629588	49.45
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	11.225	1370832	37548939	99.83
2	13.483	2794	63849	0.17
Total				100.00

Compound 2b



White solid, 83% yield, >99% ee, mp = 126-127 °C, α_D^{25}= -85 (*c* 0.15, $CHCl_3$).

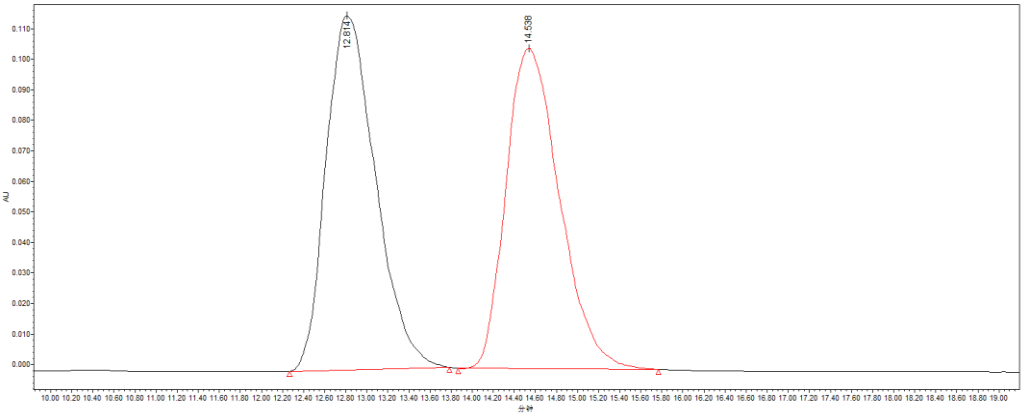
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 2.93 (t, *J* = 16.3 Hz, 1H), 2.67 (d, *J* = 17.5 Hz, 1H), 2.34 (s, 3H), 1.64 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.37, 159.07, 137.97, 134.92, 134.69, 128.03, 124.26, 120.36, 89.63, 80.85, 40.08, 28.42, 25.12, 24.74, 20.68.

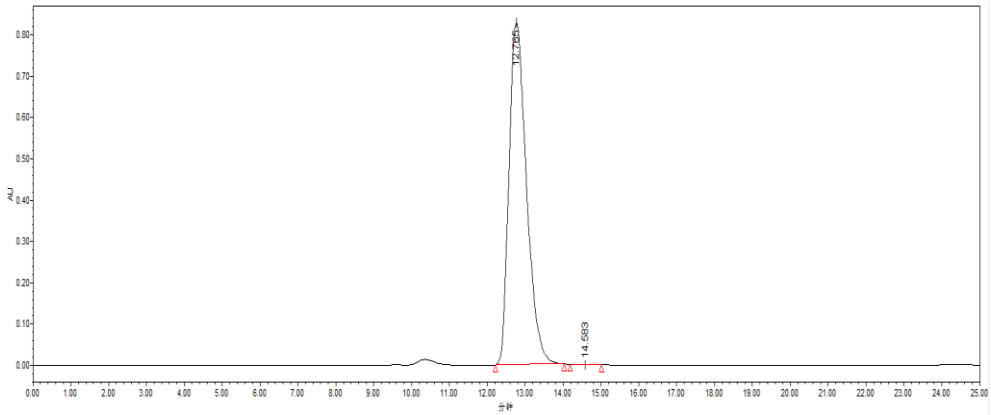
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.31.

HRMS (ESI^+, m/z): calcd for $C_{21}H_{31}BNO_5$ ($[M+H]^+$): 388.2289, found: 388.2292.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min):12.765 (major) and 14.583 (minor).

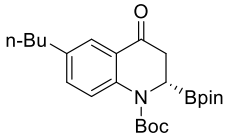


Peak ID	Ret. time	Height	Area	Area%
1	12.814	115965	3794053	50.55
2	14.538	105028	3711520	49.45
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	12.765	826641	26646714	99.99
2	14.583	137	3308	0.01
Total				100.00

Compound 2c



White solid, 65% yield, 98% ee, mp = 114-115 °C, α_D^{25}= -90 (*c* 0.10, $CHCl_3$).

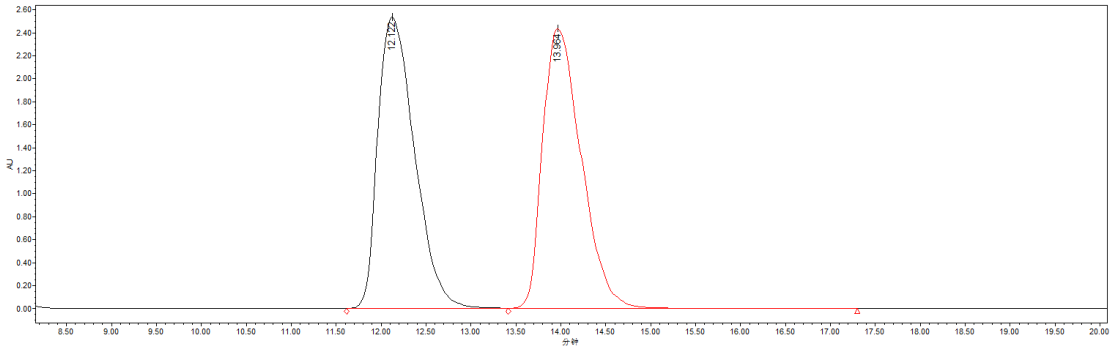
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.84 (m, 1H), 7.48 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.31 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.42 (dd, *J* = 14.9, 3.6 Hz, 1H), 2.94 – 2.90 (m, 1H), 2.72 – 2.66 (m, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.66 (s, 9H), 1.62 – 1.56 (m, 2H), 1.41 – 1.31 (m, 2H), 1.23 (s, 12H), 0.96 – 0.89 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.44, 159.10, 139.71, 138.10, 134.34, 127.42, 124.30, 120.32, 89.66, 80.84, 40.10, 34.84, 33.27, 28.44, 25.12, 24.74, 22.27, 13.89.

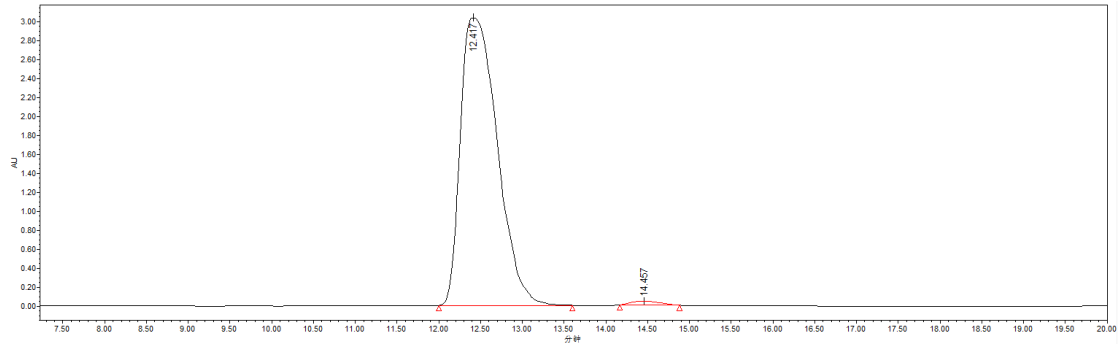
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.17.

HRMS (ESI^+, m/z): calcd for $C_{24}H_{37}BNO_5$ ($[M+H]^+$): 430.2759, found: 430.2764.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 12.417 (major) and 14.457 (minor).

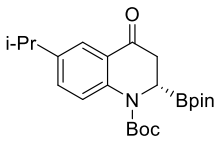


Peak ID	Ret. time	Height	Area	Area%
1	12.122	2538363	72225620	49.76
2	13.964	2435072	72931777	50.24
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	12.417	3032599	92881956	99.02
2	14.457	39849	922425	0.98
Total				100.00

Compound 2d



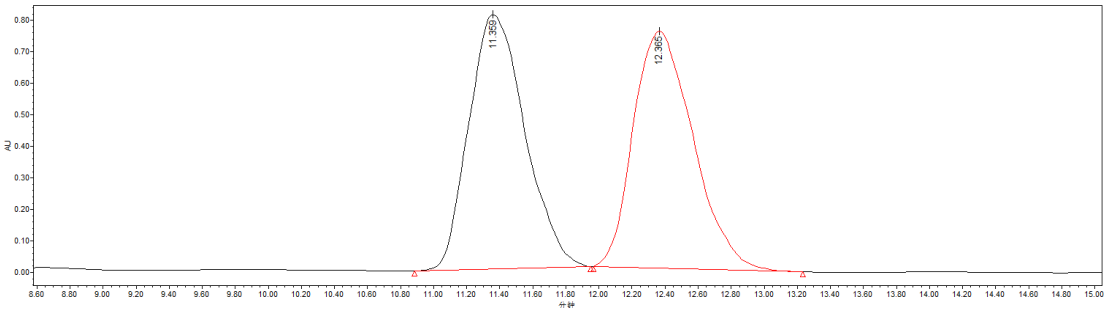
White solid, 78% yield, 98% ee, mp = 126-127 °C, α_D^{25}= -102 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.3 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.37 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.42 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.99 – 2.88 (m, 2H), 2.69 (dd, *J* = 17.7, 3.6 Hz, 1H), 1.66 (s, 9H), 1.27 - 1.22 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.44, 159.12, 145.56, 138.17, 132.56, 125.53, 124.34, 120.41, 89.69, 80.83, 40.12, 33.54, 28.44, 25.12, 24.74, 23.72, 23.69.

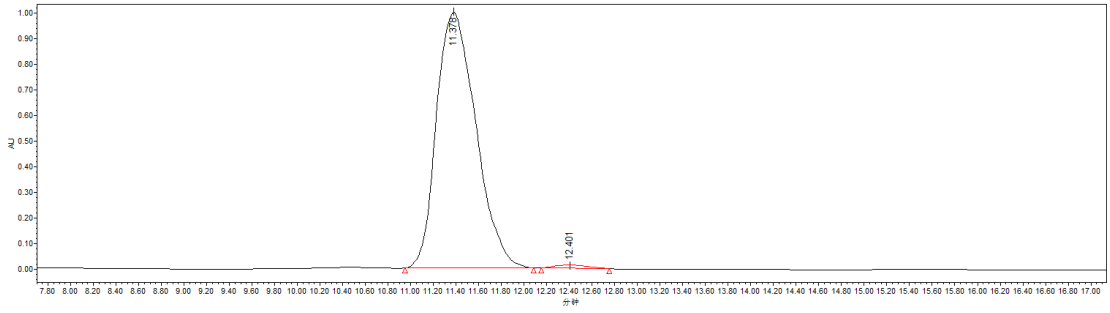
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.41.

HRMS (ESI^+, m/z): calcd for $C_{23}H_{35}BNO_5$ ($[M+H]^+$): 416.2602, found: 416.2603.

HPLC analysis: Daicel Chiralpak IC column, hexane/iPrOH = 90:10, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 11.378 (major) and 12.401 (minor).

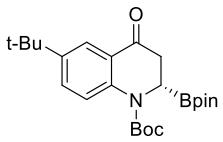


Peak ID	Ret. time	Height	Area	Area%
1	11.359	808751	19022405	50.18
2	12.365	751943	18885187	49.82
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	11.378	999807	24128165	99.00
2	12.401	12274	244532	1.00
Total				100.00

Compound 2e



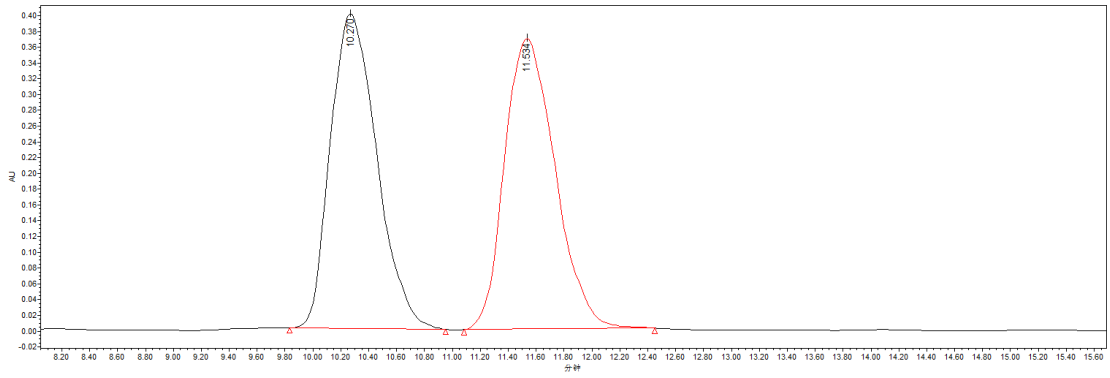
White solid, 73% yield, 98% ee, mp = 88-89 °C, α_D^{25}= -108 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 3.42 (dd, *J* = 15.0, 3.3 Hz, 1H), 2.94 (dd, *J* = 17.7, 15.1 Hz, 1H), 2.69 (dd, *J* = 17.7, 3.5 Hz, 1H), 1.66 (s, 9H), 1.33 (s, 9H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.45, 159.16, 147.90, 137.86, 131.50, 124.54, 123.97, 120.09, 89.73, 80.83, 40.11, 34.59, 31.12, 28.45, 25.13, 24.75.

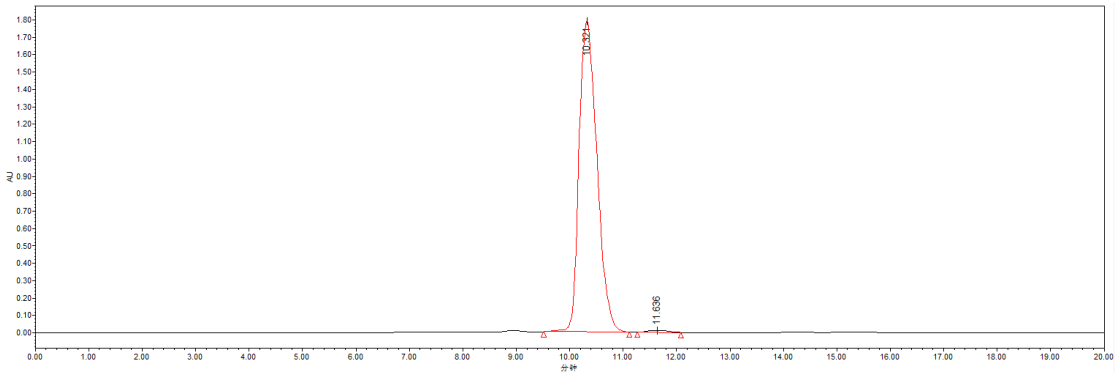
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.12.

HRMS (ESI$^+$, m/z): calcd for $C_{24}H_{37}BNO_5$ ([M+H]$^+$): 430.2759, found: 430.2767.

HPLC analysis: Daicel Chiralpak IC column, hexane/iPrOH = 90:10, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 10.321 (major) and 11.636 (minor).

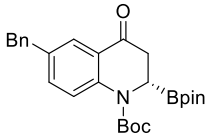


Peak ID	Ret. time	Height	Area	Area%
1	10.270	399834	9240957	49.93
2	11.534	368785	9266801	50.07
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	10.321	1784698	41502871	99.30
2	11.636	11356	290759	0.70
Total				100.00

Compound 2f



White solid, 70% yield, 95% ee, mp = 118-119 °C, α_D^{25}= -65 (*c* 0.10, $CHCl_3$).

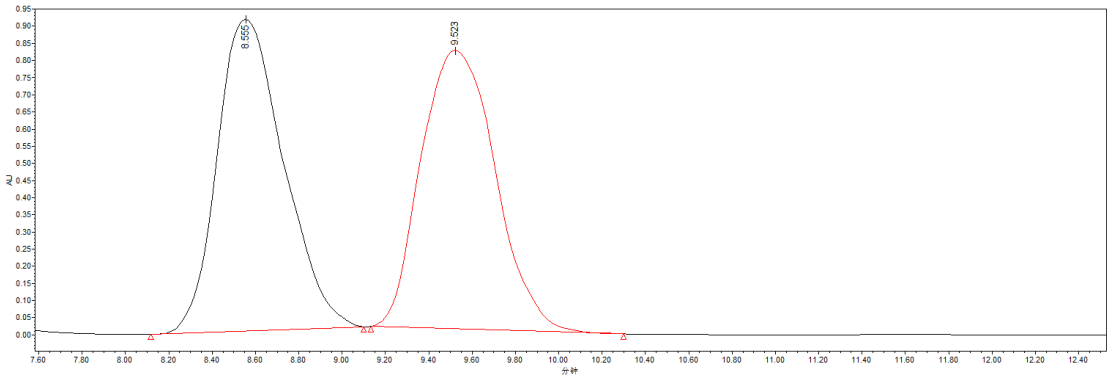
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.32 – 7.28 (m, 3H), 7.23 – 7.18 (m, 3H), 3.97 (s, 2H), 3.41 (dd, *J* = 15.0, 3.3 Hz, 1H), 2.93 (dd, *J* = 17.7, 15.1 Hz, 1H), 2.68 (dd, *J* = 17.8, 3.5 Hz, 1H), 1.64 (s, 9H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.25, 159.09, 140.11, 138.54, 138.06, 134.62, 128.91, 128.68, 127.96, 126.44, 124.39, 120.65, 89.82, 80.91, 41.23, 40.06, 28.43, 25.12, 24.74.

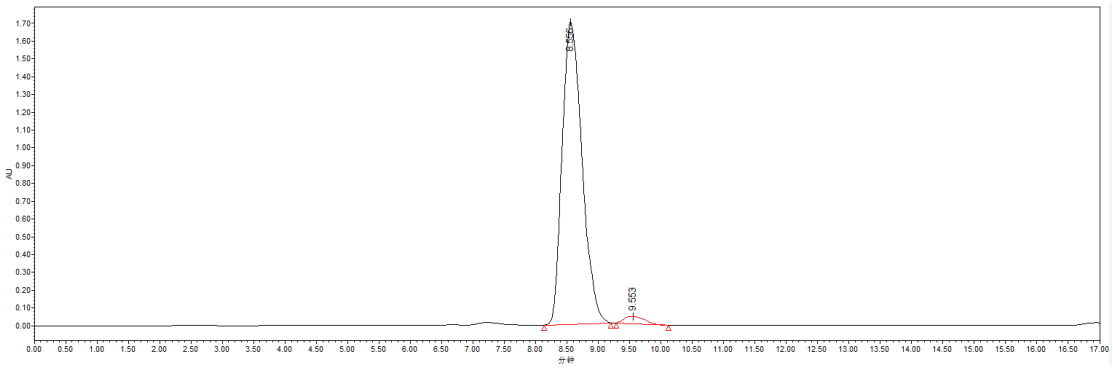
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.25.

HRMS (ESI^+, m/z): calcd for $C_{27}H_{35}BNO_5$ ($[M+H]^+$): 464.2602, found: 464.2624.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 90:10, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 8.556 (major) and 9.553 (minor).

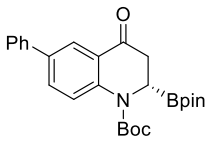


Peak ID	Ret. time	Height	Area	Area%
1	8.555	908562	19397676	49.98
2	9.523	813422	19414870	50.02
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	8.556	1699749	37459458	97.69
2	9.553	41305	887345	2.31
Total				100.00

Compound 2g



White solid, 83% yield, 91% ee, mp = 104-105 °C, α_D^{25}= -58 (*c* 0.10, $CHCl_3$).

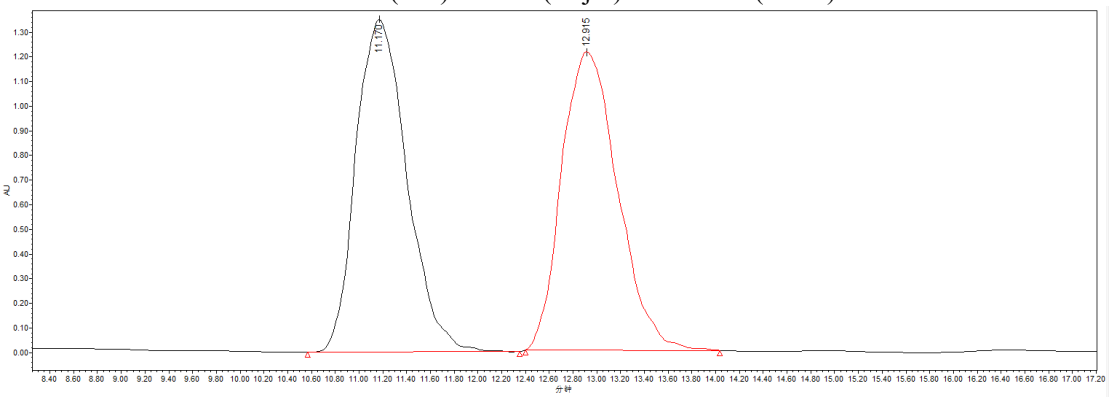
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.5 Hz, 1H), 7.75 – 7.72 (m, 4H), 7.46 – 7.34 (m, 3H), 3.48 (dd, *J* = 14.8, 2.7 Hz, 1H), 3.03 – 3.94 (m, 1H), 2.73 (dd, *J* = 17.7, 3.3 Hz, 1H), 1.68 (s, 9H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.09, 159.06, 139.48, 139.17, 137.70, 132.51, 128.94, 127.80, 126.84, 126.25, 124.71, 121.00, 89.88, 40.09, 28.46, 25.13, 24.76.

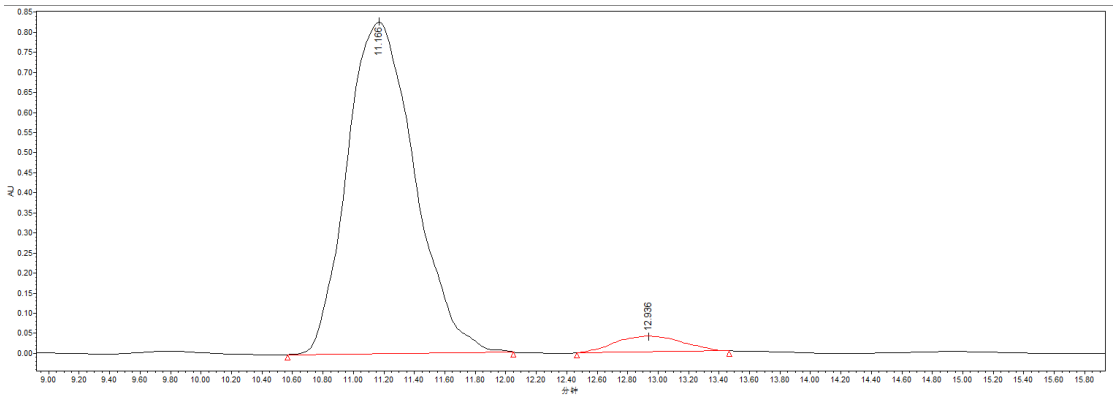
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.44.

HRMS (ESI^+, m/z): calcd for $C_{26}H_{32}BNO_5$ ($[M+H]^+$): 450.2446, found: 450.2453.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 90:10, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 11.166 (major) and 12.936 (minor).

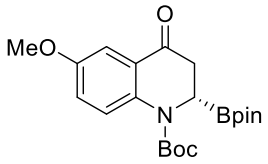


Peak ID	Ret. time	Height	Area	Area%
1	11.170	1349450	40170902	50.28
2	12.915	1211144	39729394	49.72
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	11.166	826456	25412505	95.51
2	12.936	39039	1193276	4.49
Total				100.00

Compound 2h



White solid, 86% yield, 95% ee, mp = 125-126 °C, α_D^{25}= -117 (*c* 0.10, $CHCl_3$).

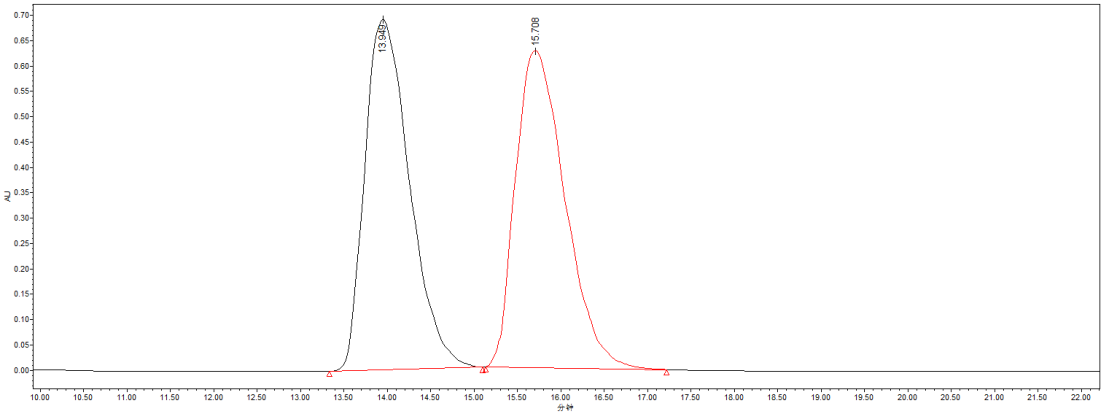
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.05 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.82 (s, 3H), 3.40 (dd, *J* = 14.6, 2.2 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.68 (dd, *J* = 17.8, 3.4 Hz, 1H), 1.63 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.11, 158.93, 156.56, 134.00, 125.42, 122.09, 122.00, 109.73, 89.55, 80.85, 55.66, 40.06, 28.44, 25.12, 24.73.

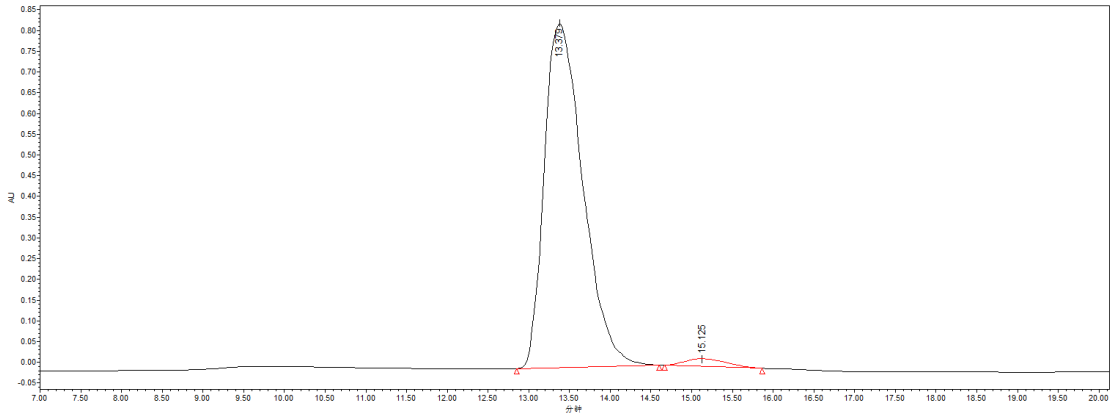
^{11}B NMR (128 MHz, $CDCl_3$) δ 14.32.

HRMS (ESI^+, m/z): calcd for $C_{21}H_{31}BNO_6$ ($[M+H]^+$): 404.2238, found: 404.2253.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min):13.379 (major) and 15.125 (minor).

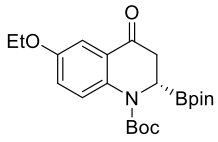


Peak ID	Ret. time	Height	Area	Area%
1	13.949	690267	24752182	50.11
2	15.708	624239	24644427	49.89
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	13.379	830165	27337011	97.71
2	15.125	18302	641153	2.29
Total				100.00

Compound 2i



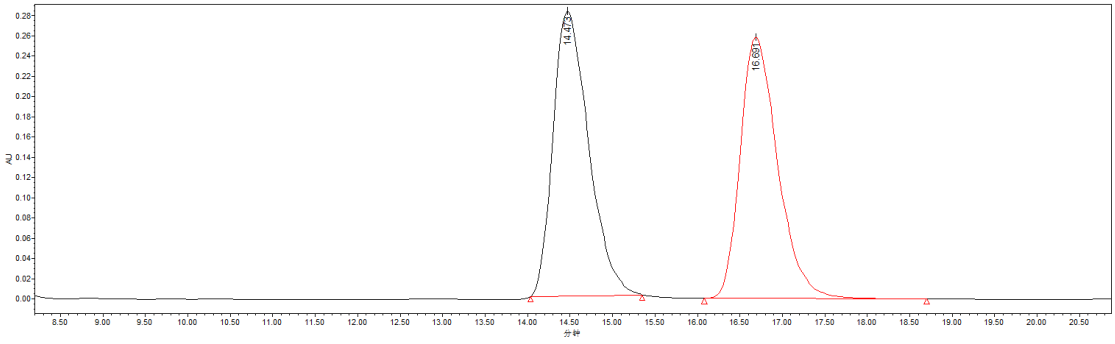
White solid, 81% yield, 96% ee, mp = 117-118 °C, α_D^{25}= -125 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 2H), 7.05 (dd, *J* = 9.1, 3.1 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.41 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.94 (dd, *J* = 17.8, 14.9 Hz, 1H), 2.69 (dd, *J* = 17.8, 3.7 Hz, 1H), 1.64 (s, 9H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.17, 158.95, 155.94, 133.83, 125.41, 122.48, 121.96, 110.39, 89.53, 63.95, 40.09, 28.45, 25.13, 24.74, 14.70.

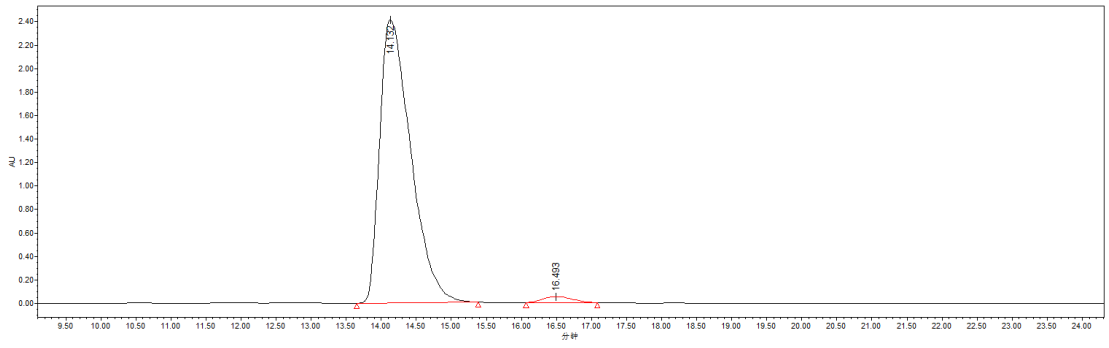
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.04.

HRMS (ESI^+, m/z): calcd for $C_{22}H_{33}BNO_6$ ($[M+H]^+$): 418.2395, found: 418.2395.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min):14.132 (major) and 16.493 (minor).

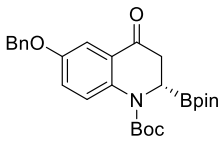


Peak ID	Ret. time	Height	Area	Area%
1	14.473	281734	8198631	50.87
2	16.691	258240	7918871	49.13
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	14.132	2408501	74312973	98.00
2	16.493	52107	1516028	2.00
Total				100.00

Compound 2j



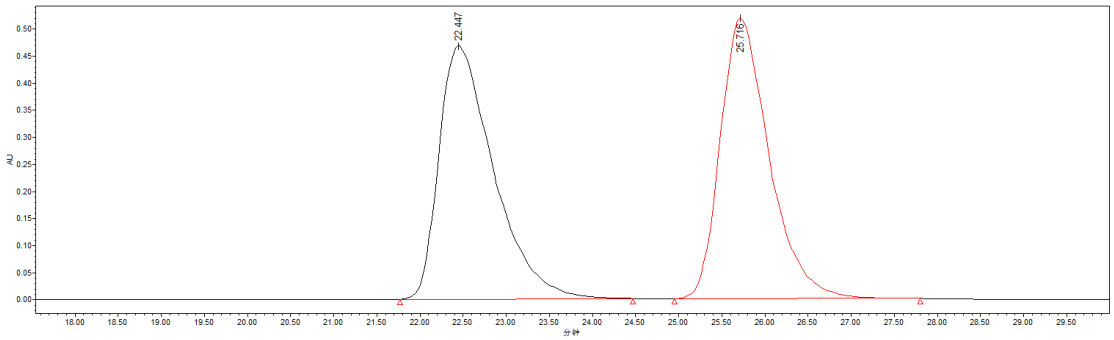
White solid, 73% yield, 92% ee, mp = 108-109 °C, α_D^{25}= -106 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 3.1 Hz, 1H), 7.42 (d, *J* = 9.1 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.06 (dd, *J* = 9.1, 3.1 Hz, 1H), 5.01 (s, 2H), 3.34 (dd, *J* = 14.9, 3.3 Hz, 1H), 2.87 (dd, *J* = 17.8, 15.0 Hz, 1H), 2.62 (dd, *J* = 17.8, 3.6 Hz, 1H), 1.57 (s, 9H), 1.16 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.06, 158.96, 155.72, 136.31, 134.15, 128.67, 128.21, 127.61, 125.41, 122.69, 122.05, 110.87, 89.68, 80.85, 70.37, 40.06, 28.45, 25.14, 24.74.

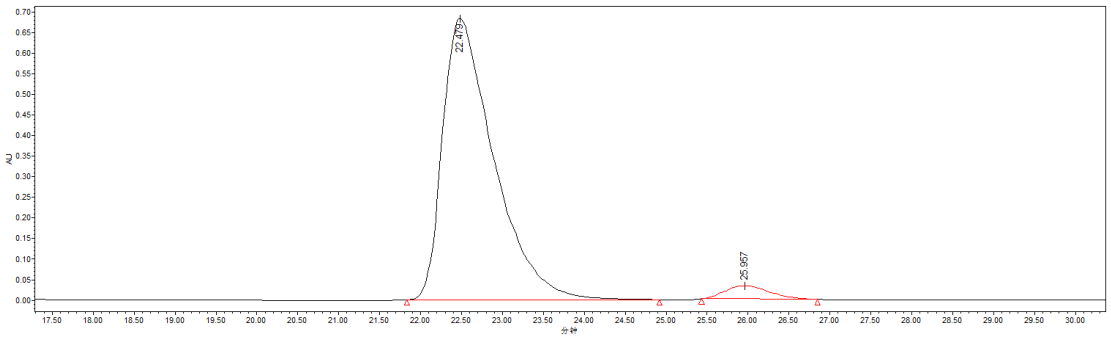
^{11}B NMR (128 MHz, $CDCl_3$) δ 14.02.

HRMS (ESI^+, m/z): calcd for $C_{27}H_{35}BNO_6$ ($[M+H]^+$): 480.2551, found: 480.2539.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 22.479 (major) and 25.957 (minor).

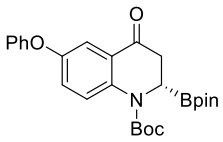


Peak ID	Ret. time	Height	Area	Area%
1	22.447	468200	20579611	50.18
2	25.7146	517547	20435307	49.82
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	22.479	682753	29731220	96.06
2	25.957	32640	1219645	3.94
Total				100.00

Compound 2k



White solid, 70% yield, 91% ee, mp = 92-93 °C, α_D^{25}= -96 (*c* 0.15, $CHCl_3$).

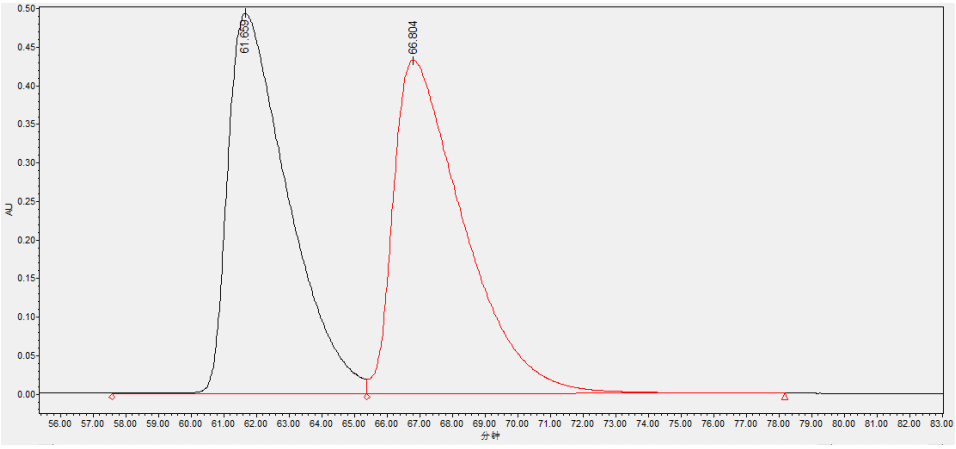
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.36 – 7.33 (m, 2H), 7.15 – 7.11 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.42 (dd, *J* = 14.7, 2.4 Hz, 1H), 2.93 (dd, *J* = 17.6, 15.1 Hz, 1H), 2.68 (dd, *J* = 17.8, 3.4 Hz, 1H), 1.64 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.48, 158.84, 156.37, 154.50, 135.75, 129.98, 125.86, 124.48, 124.01, 122.28, 119.28, 116.45, 89.57, 81.04, 40.04, 28.44, 25.10, 24.75.

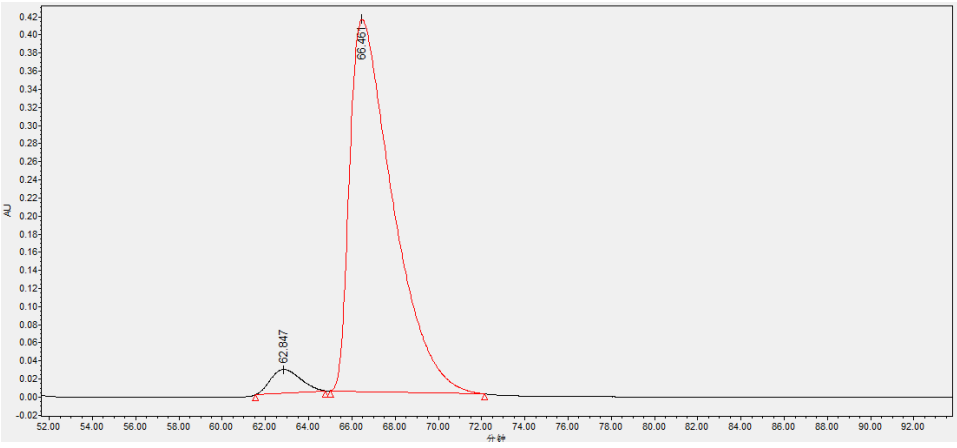
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.73.

HRMS (ESI^+, m/z): calcd for $C_{26}H_{33}BNO_6$ ($[M+H]^+$): 466.2395, found: 466.2402.

HPLC analysis: Daicel Chiralpak IC column, hexane/iPrOH = 98:2, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 66.46 (major) and 62.84 (minor).

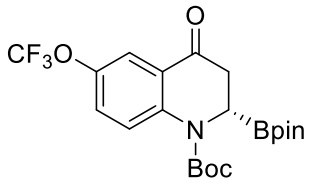


Peak ID	Ret. time	Height	Area	Area%
1	61.659	493405	63155690	49.37
2	66.804	432579	64766558	50.63
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	62.847	26299	2523391	4.25
2	66.461	410711	56905253	95.75
Total				100.00

Compound 2l



White solid, 80% yield, 93% ee, mp = 108-109 °C, α_D^{25}= -62 (*c* 0.10, $CHCl_3$).

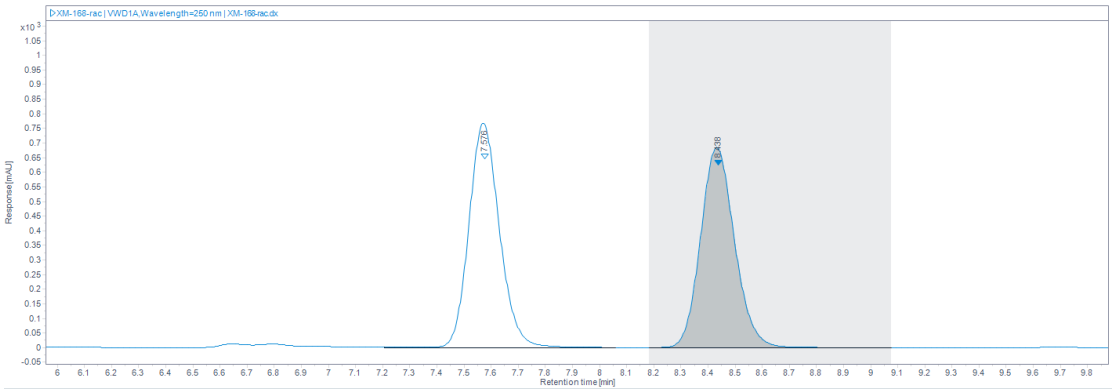
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.62 (d, *J* = 4.8 Hz, 1H), 7.34 (s, 1H), 3.48 – 3.46 (m, 1H), 2.98 – 2.90 (m, 1H), 2.75 – 2.69 (m, 1H), 1.65 (s, 9H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.07, 159.07, 140.42, 134.08, 125.78 (q, *J* = 262.6 Hz), 124.83, 124.54, 120.56, 89.78, 80.98, 40.07, 28.43, 25.12, 24.74.

^{11}B NMR (128 MHz, $CDCl_3$) δ 15.19.

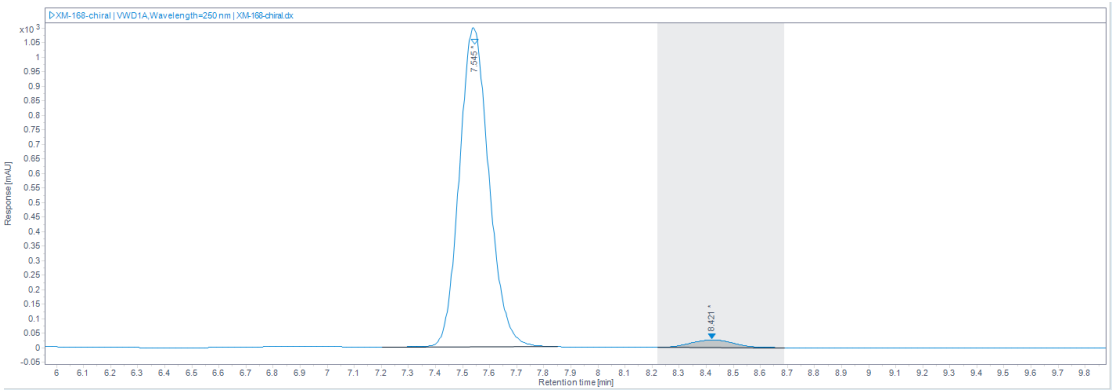
HRMS (ESI^+, m/z): calcd for $C_{21}H_{28}BF_3NO_6$ ($[M+H]^+$): 458.1956, found: 458.1954.

HPLC analysis: Daicel Chiralpak ADH column, hexane/iPrOH = 92:8, flow rate = 0.5 mL/min, 25 °C, detection at 254 nm. Retention time (min):7.54 (major) and 8.42 (minor).



Peaks Summary

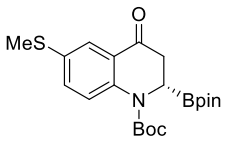
#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	7.576	6018.328	50.249	7.207	8.058		1.00525
2	8.438	5958.582	49.751	8.182	9.076	3.95640	0.97305



Peaks Summary

#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	7.545	8375.404	96.733	7.204	7.850		1.02719
2	8.421	282.884	3.267	8.221	8.690	3.59581	0.89516

Compound 2m



White solid, 72% yield, 91% ee, mp = 112-113 °C, α_D^{25}= -70 (*c* 0.10, $CHCl_3$).

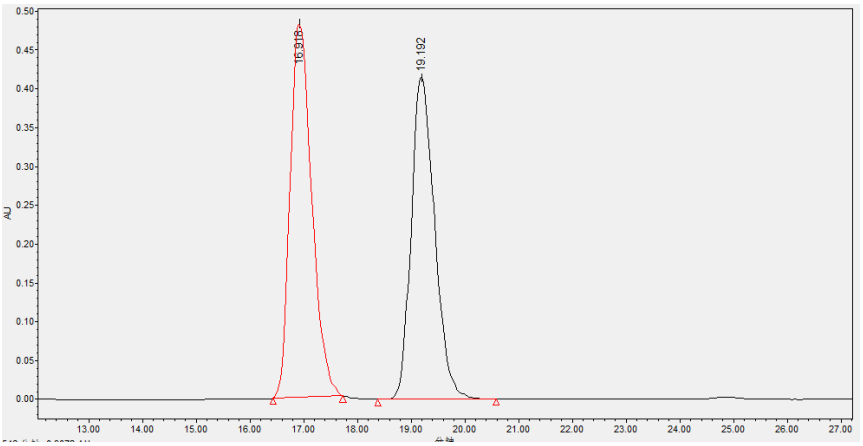
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.3 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.35 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.40 (dd, *J* = 14.9, 3.3 Hz, 1H), 2.96 – 2.92 (m, 1H), 2.68 (dd, *J* = 17.8, 3.6 Hz, 1H), 2.49 (s, 3H), 1.63 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.69, 158.91, 137.63, 135.64, 132.34, 124.81, 124.79, 121.03, 89.80, 81.02, 39.99, 28.42, 25.12, 24.74, 15.80.

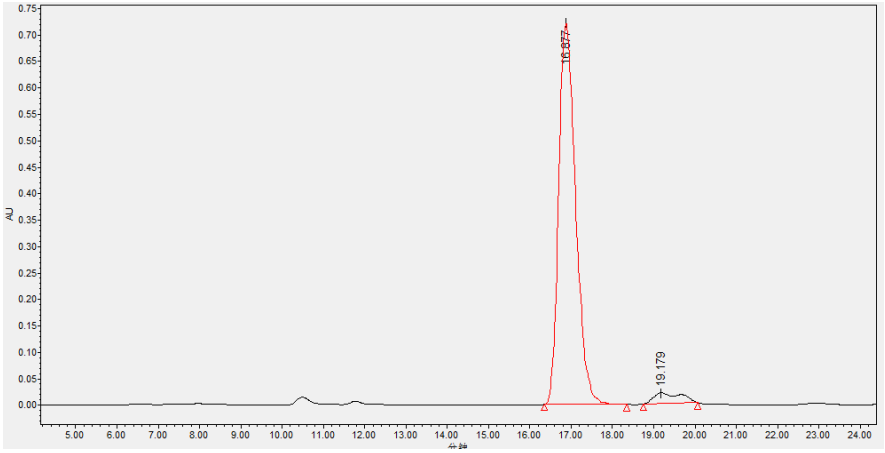
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.76.

HRMS (ESI^+, m/z): calcd for $C_{21}H_{31}BNO_5S$ ($[M+H]^+$): 420.2010, found: 420.2007.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 90:10, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 11.166 (major) and 12.936 (minor).

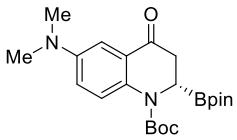


Peak ID	Ret. time	Height	Area	Area%
1	16.918	480791	13442830	51.69
2	19.192	414740	12565639	48.31
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	16.877	720604	20560095	95.60
2	19.179	19990	946822	4.4
Total				100.00

Compound 2n



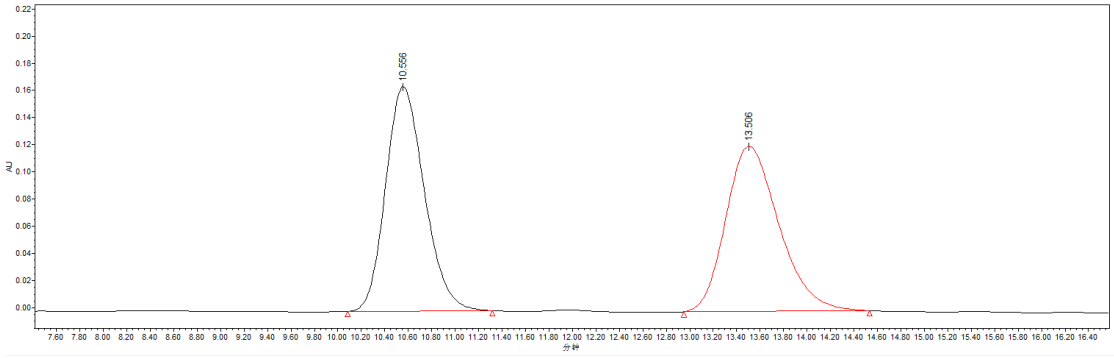
Yellow solid, 64% yield, 98% ee, mp = 104-105 °C, α_D^{25}= -165 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 9.1 Hz, 1H), 7.31 (d, *J* = 3.3 Hz, 1H), 6.88 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.38 (dd, *J* = 15.0, 3.6 Hz, 1H), 3.04 – 2.88 (m, 7H), 2.67 (dd, *J* = 17.8, 3.6 Hz, 1H), 1.65 (s, 9H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.90, 158.95, 147.65, 129.98, 125.02, 121.29, 118.18, 109.85, 89.25, 80.59, 40.53, 40.30, 28.47, 25.13, 24.73.

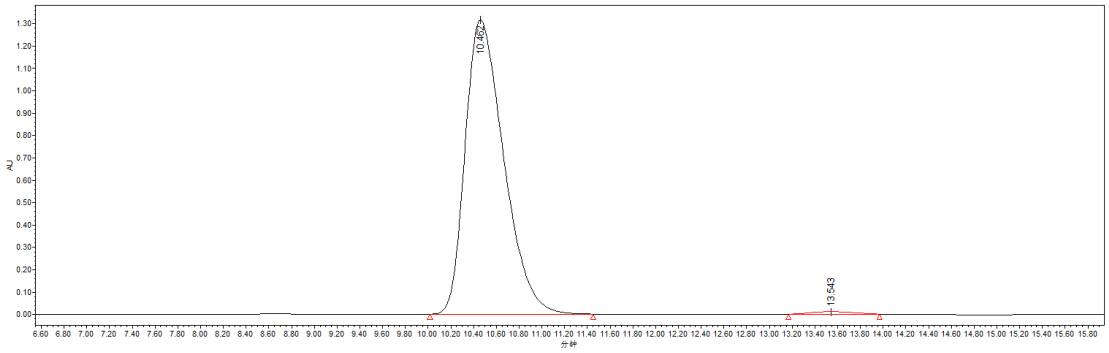
^{11}B NMR (128 MHz, $CDCl_3$) δ 14.14.

HRMS (ESI^+, m/z): calcd for $C_{22}H_{34}BN_2O_5$ $[M+H]^+$: 417.2555, found: 417.2558.

HPLC analysis: Daicel Chiralpak IC column, hexane/iPrOH = 90:10, flow rate = 2.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 10.462 (major) and 13.543 (minor).

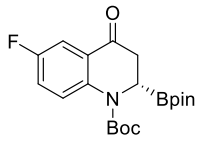


Peak ID	Ret. time	Height	Area	Area%
1	10.556	165285	3782975	49.81
2	13.506	121563	3812502	50.19
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	10.462	1315126	30936708	99.06
2	13.543	11308	293778	0.94
Total				100.00

Compound 2o



White solid, 78% yield, >99% ee, mp = 98-99 °C, α_D^{25}= -111 (*c* 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.57 (dd, *J* = 9.1, 4.4 Hz, 1H), 7.21 – 7.16 (m, 1H), 3.45 (dd, *J* = 14.7, 3.5 Hz, 1H), 2.95 (dd, *J* = 17.9, 14.8 Hz, 1H), 2.71 (dd, *J* = 17.9, 3.6 Hz, 1H), 1.65 (s, 9H), 1.24 (s, 12H).

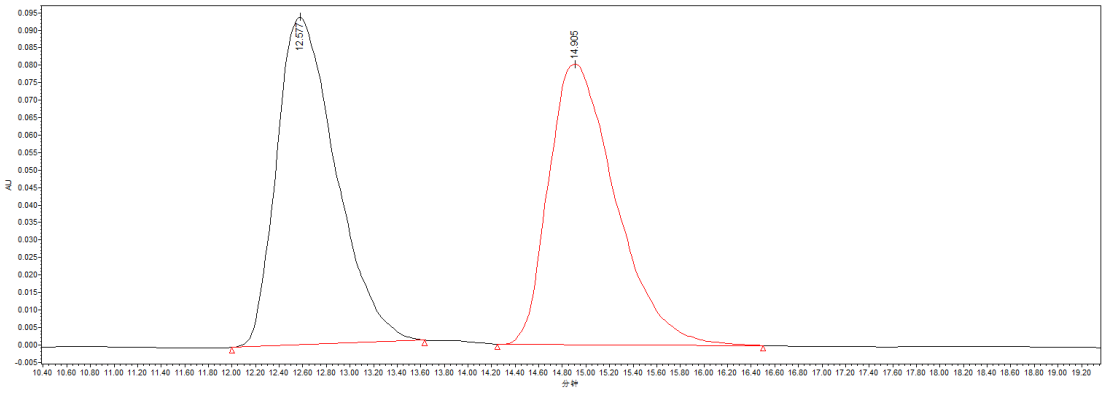
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.03, 159.4 (d, *J* = 248.4 Hz), 158.73, 136.78, 126.17 (d, *J* = 6.0 Hz), 122.72(d, *J* = 7.0 Hz), 121.21 (d, *J* = 23.2 Hz), 113.86 (d, *J* = 23.2 Hz), 89.77, 81.16, 39.91, 28.40, 25.10, 24.71.

^{11}B NMR (128 MHz, $CDCl_3$) δ 16.45.

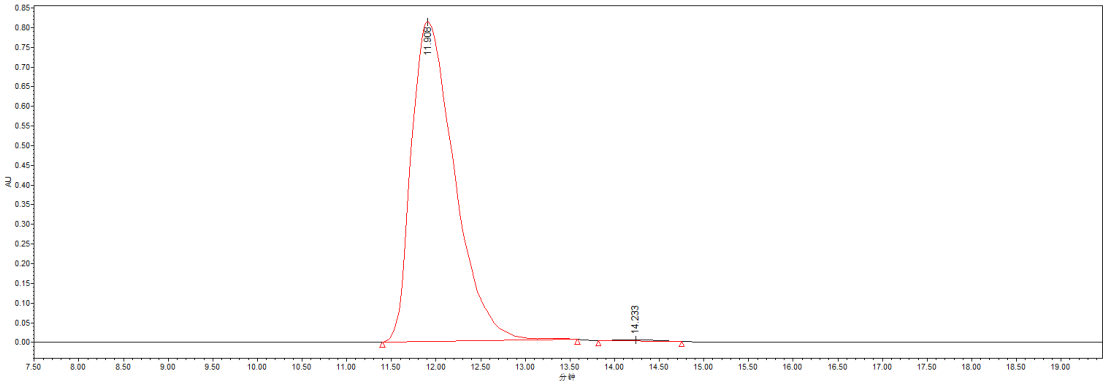
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.97.

HRMS (ESI^+, m/z): calcd for $C_{20}H_{28}BFNO_5$ ($[M+H]^+$): 392.2039, found: 392.2050.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 98:2, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 11.908 (major) and 14.233 (minor).

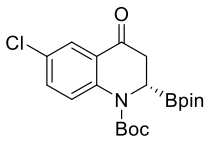


Peak ID	Ret. time	Height	Area	Area%
1	12.577	93826	3274186	50.85
2	14.905	80300	3164376	49.15
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	11.908	812860	2731239	99.65
2	14.233	3314	97004	0.35
Total				100.00

Compound 2p



White solid, 60% yield, 97% ee, mp = 84-85 °C, α_D^{25}= -108 (*c* 0.10, $CHCl_3$).

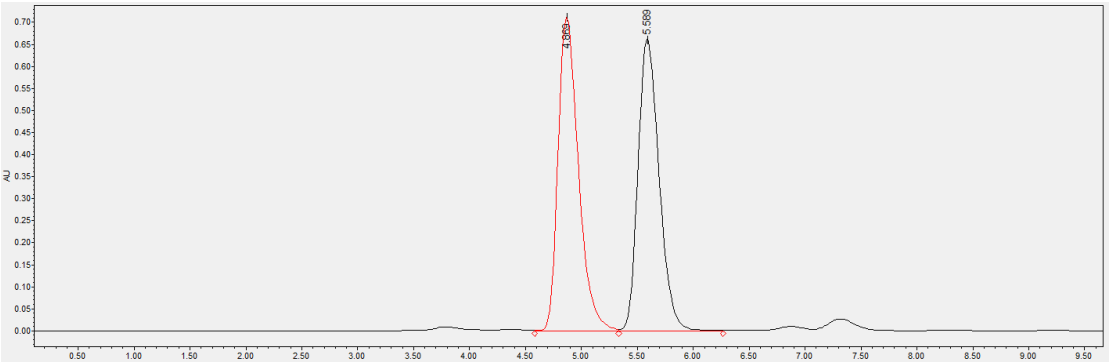
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.7 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.43 (dd, *J* = 8.8, 1.9 Hz, 1H), 3.44 – 3.41 (m, 1H), 2.96 – 2.88 (m, 1H), 2.69 (dd, *J* = 17.8, 3.2 Hz, 1H), 1.64 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.86, 158.69, 139.08, 133.87, 130.73, 127.74, 125.62, 122.27, 89.91, 39.85, 28.40, 25.10, 24.73.

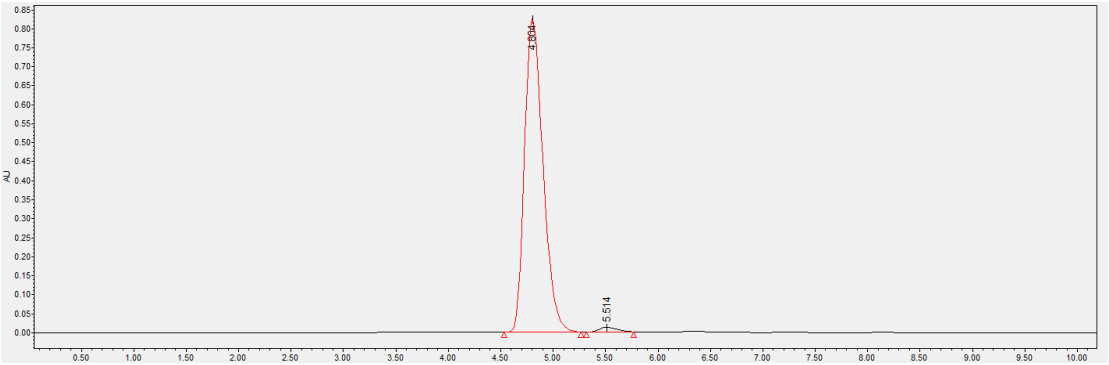
^{11}B NMR (128 MHz, $CDCl_3$) δ 16.71.

HRMS (ESI^+, m/z): calcd for $C_{20}H_{28}BClNO_5$ ($[M+H]^+$): 408.1743, found: 408.1725.

HPLC analysis: Daicel Chiralpak ADH column, hexane/iPrOH =90:10, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 4.804 (major) and 5.514 (minor).

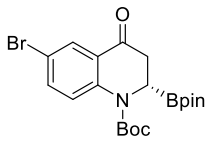


Peak ID	Ret. time	Height	Area	Area%
1	4.869	711567	9031035	50.96
2	5.589	663087	8689887	49.04
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	4.804	825700	10159673	98.56
2	5.514	12307	148375	1.44
Total				100.00

Compound 2q



White solid, 68% yield, 98% ee, mp = 98-99 °C, α_D^{25}= -95 (*c* 0.10, $CHCl_3$).

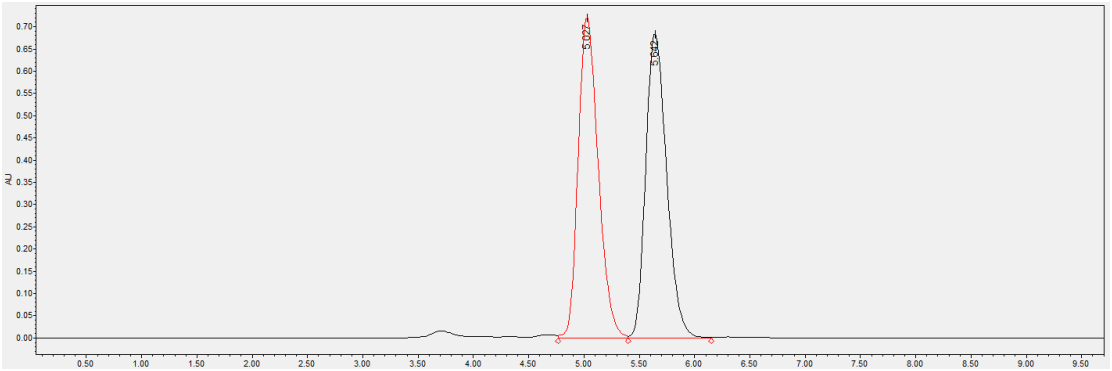
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 3.43 (dd, *J* = 14.8, 3.3 Hz, 1H), 2.92 (dd, *J* = 17.8, 14.8 Hz, 1H), 2.69 (dd, *J* = 17.8, 3.6 Hz, 1H), 1.64 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.74, 158.66, 139.54, 136.75, 130.79, 125.82, 122.51, 118.27, 89.97, 81.29, 39.80, 28.39, 25.09, 24.72.

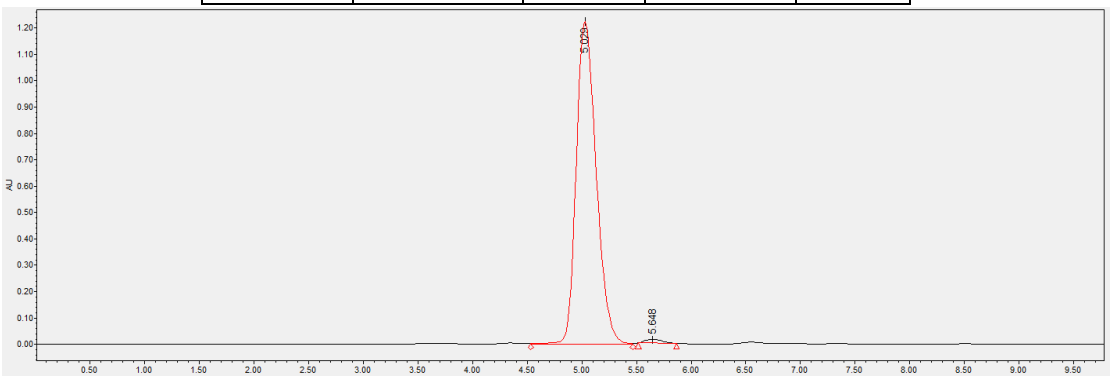
^{11}B NMR (128 MHz, $CDCl_3$) δ 16.00.

HRMS (ESI^+, m/z): calcd for $C_{20}H_{28}BBrNO_5$ ($[M+H]^+$): 452.1238, found: 452.1253.

HPLC analysis: Daicel Chiralpak ADH column, hexane/iPrOH = 90:10, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 5.029 (major) and 5.648 (minor).

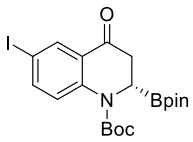


Peak ID	Ret. time	Height	Area	Area%
1	5.027	721100	9112576	50.19
2	5.642	685688	9041780	49.81
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	5.029	1226343	15566455	99.05
2	5.648	13791	149433	0.95
Total				100.00

Compound 2r



White solid, 57% yield, 96% ee, mp = 92-93 °C, α_D^{25}= -90 (*c* 0.10, $CHCl_3$).

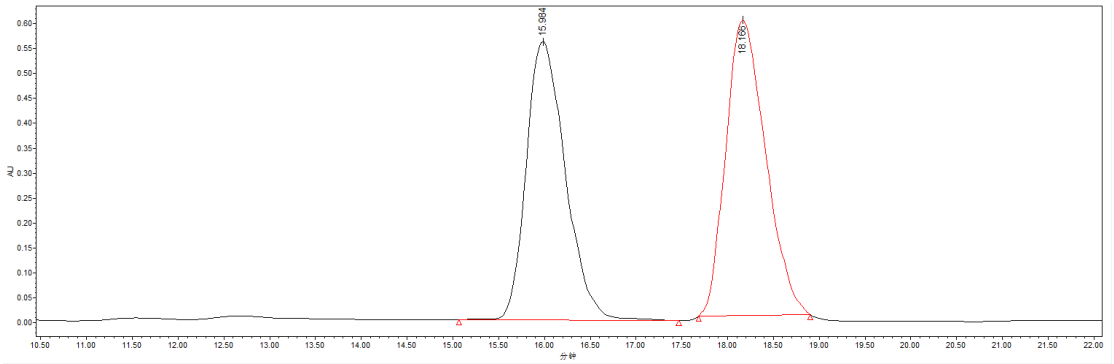
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.3 Hz, 1H), 7.78 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 3.43 (dd, *J* = 14.8, 3.5 Hz, 1H), 2.93 (dd, *J* = 17.8, 14.8 Hz, 1H), 2.69 (dd, *J* = 17.8, 3.6 Hz, 1H), 1.65 (s, 9H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.69, 158.69, 142.56, 140.19, 136.88, 125.89, 122.62, 90.01, 88.72, 81.28, 39.75, 28.40, 25.10, 24.73.

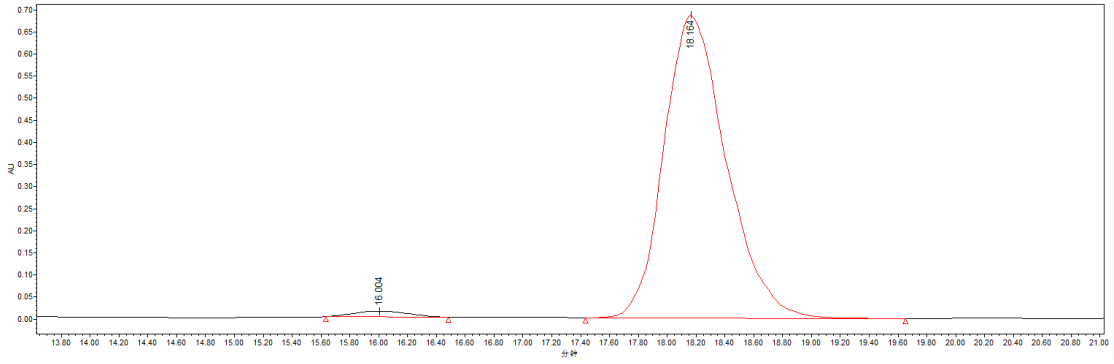
^{11}B NMR (128 MHz, $CDCl_3$) δ 16.64.

HRMS (ESI^+, m/z): calcd for $C_{20}H_{28}BINO_5$ ($[M+H]^+$): 500.1099, found: 500.1097.

HPLC analysis: Daicel Chiralpak IC column, hexane/iPrOH = 95:5, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 16.004 (minor) and 18.164 (major).

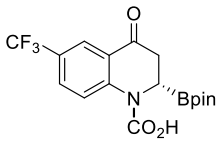


Peak ID	Ret. time	Height	Area	Area%
1	15.984	558725	16553802	48.04
2	18.166	592175	17904514	51.96
Total				100.00

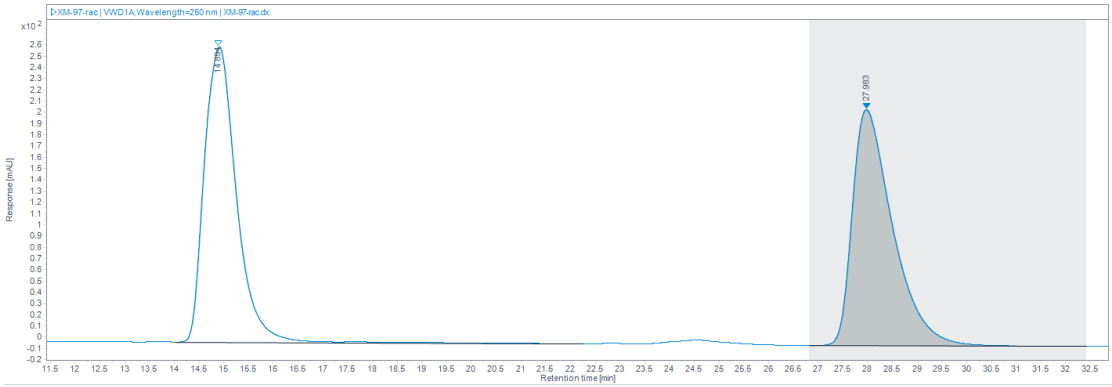


Peak ID	Ret. time	Height	Area	Area%
1	16.004	13084	340810	1.63
2	18.164	685476	20523579	98.37
Total				100.00

Compound 2s

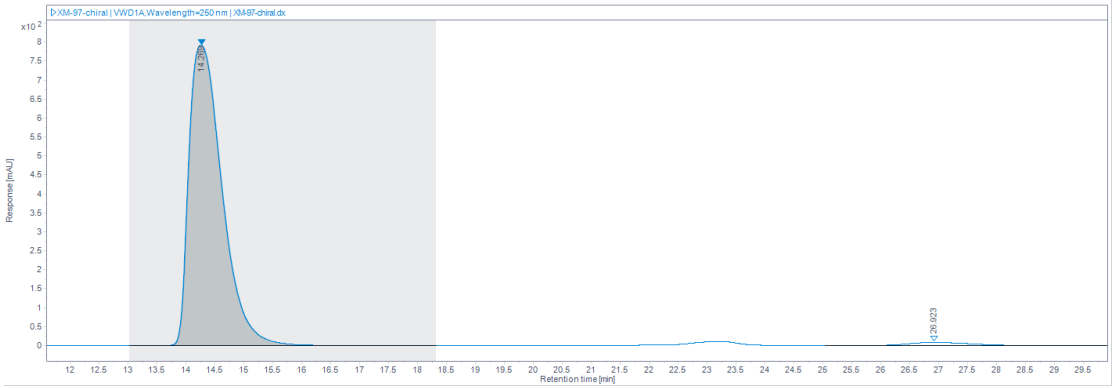


White solid, 70% yield, 96% ee, mp = 180-181 °C, α_D^{25}= -90 (*c* 0.10, CH_3OH).
^{1}H NMR (400 MHz, MeOD) δ 8.54 (d, *J* = 8.9 Hz, 1H), 8.12 (s, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 3.17 (dd, *J* = 16.1, 3.3 Hz, 1H), 2.72 (t, *J* = 16.5 Hz, 1H), 2.51 (dd, *J* = 17.0, 3.3 Hz, 1H), 1.31 – 1.04 (m, 12H).
^{13}C NMR (101 MHz, MeOD) δ 196.34, 158.68, 147.07, 130.05 (q, *J* = 4.0 Hz), 126.92 (q, *J* = 270.6 Hz), 123.95 (q, *J* = 4.0 Hz), 122.65 (q, *J* = 33.3 Hz), 121.78, 119.69, 79.33, 79.05, 39.33, 24.53, 24.09, 23.86, 23.68.
^{11}B NMR (128 MHz, MeOD) δ 8.34.
^{19}F NMR (376 MHz, MeOD) δ -63.73.
HRMS (ESI$^-$, m/Z): calcd for $C_{17}H_{18}BF_3NO_5$ [M-H]$^-$: 384.1235, found: 384.1230.
HPLC analysis: Daicel Chiralpak ADH column, hexane/iPrOH = 85:15, flow rate = 0.4 mL/min, 25 °C, detection at 254 nm. Retention time (min): 14.26 (major) and 26.92 (minor).



Peaks | Summary

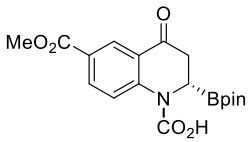
#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	14.894	11934.393	50.122	14.037	22.252		0.73223
2	27.983	11876.072	49.878	26.826	32.420		0.52530



Peaks | Summary

#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	14.269	31671.304	98.041	13.023	18.327		0.57681
2	26.923	632.848	1.959	25.042	30.090	8.37701	0.68498

Compound 2t



White solid, 65% yield, >99% ee, mp = 262-263 °C, α_D^{25} = -118 (*c* 0.10, CH_3OH).

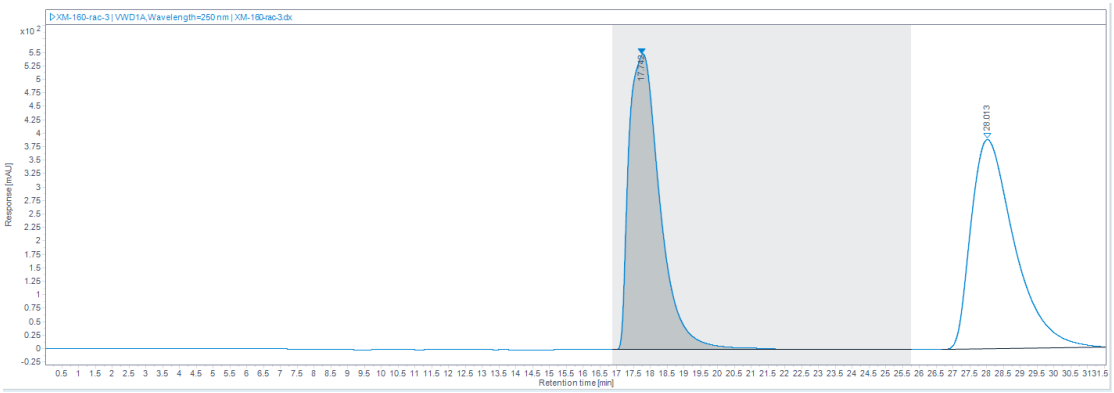
^1H NMR (400 MHz, D_2O) δ 8.20 (d, *J* = 1.9 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.97 (dd, *J* = 9.1, 2.0 Hz, 1H), 3.87 (s, 3H), 3.22 (dd, *J* = 16.0, 3.4 Hz, 1H), 2.70 (t, *J* = 16.5 Hz, 1H), 2.54 (dd, *J* = 17.2, 3.5 Hz, 1H), 1.32 – 1.03 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 196.16, 166.16, 157.24, 148.94, 134.54, 128.84, 121.40, 121.12, 118.98, 78.54, 78.35, 52.35, 39.96, 26.28, 25.84, 25.57.

^{11}B NMR (128 MHz, D_2O) δ 7.97.

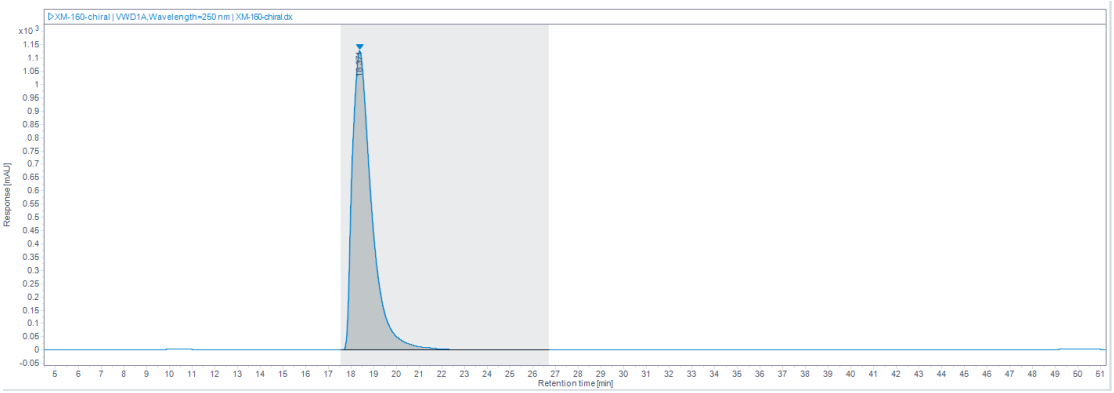
HRMS (ESI^-, m/z): calcd for $C_{18}H_{21}BNO_7$ ($[M-H]^-$): 374.1416, found: 374.1414.

HPLC analysis: Daicel Chiralpak ADH column, hexane/iPrOH = 85:15, flow rate = 0.4 mL/min, 25 °C, detection at 254 nm. Retention time (min): 18.37 (major).



Peaks | Summary

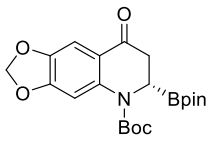
#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	17.742	35407.641	50.399	16.866	25.759		0.64536
2	28.013	34847.120	49.601	26.653	31.530		0.57137



Peaks | Summary

#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	18.371	67098.647	100.000	17.570	26.726		0.54202

Compound 2u



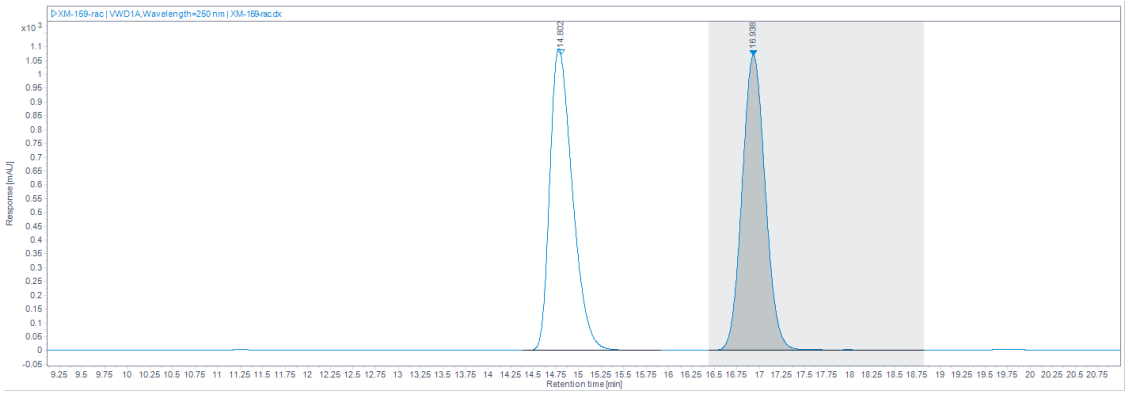
White solid, 76% yield, >99% ee, mp = 130-131 °C, α_D^{25}= -74 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.02 (s, 1H), 6.02 (dd, *J* = 4.8, 1.3 Hz, 2H), 3.39 (dd, *J* = 14.8, 3.0 Hz, 1H), 2.88 (dd, *J* = 17.8, 14.9 Hz, 1H), 2.62 (dd, *J* = 17.8, 3.7 Hz, 1H), 1.64 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.68, 158.71, 152.36, 145.15, 137.22, 119.58, 106.29, 102.15, 101.51, 89.79, 80.99, 39.62, 28.43, 25.11, 24.72.

^{11}B NMR (128 MHz, $CDCl_3$) δ 15.79.

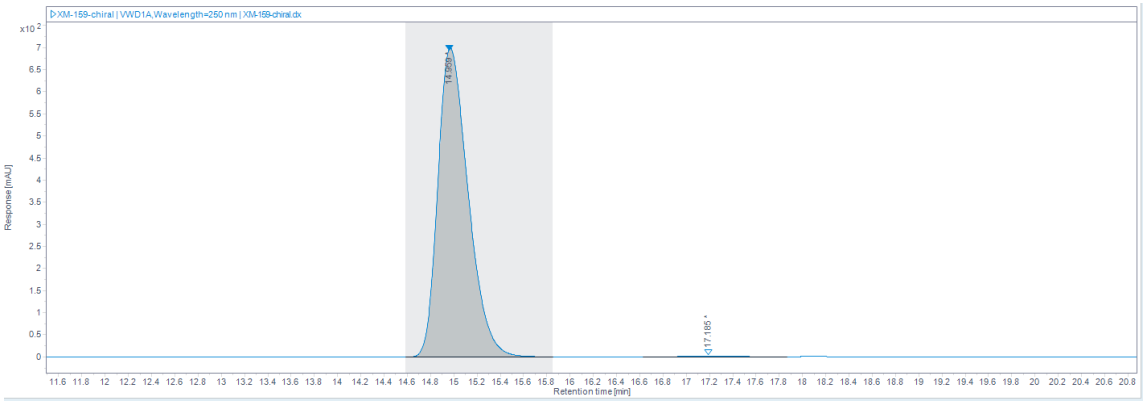
HRMS (ESI^+, m/z): calcd for $C_{21}H_{29}BNO_7$ ($[M+H]^+$): 418.2031, found: 418.2040.

HPLC analysis: Daicel Chiralpak ADH column, hexane/iPrOH = 92:8, flow rate = 0.5 mL/min, 25 °C, detection at 254 nm. Retention time (min): 14.95 (major) and 17.18 (minor).



Peaks | Summary

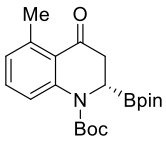
#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	14.802	18993.524	49.808	14.382	15.907		0.80208
2	16.938	19140.332	50.192	16.439	18.831	4.61418	0.91860



Peaks | Summary

#	RT (min)	Area	Area%	Start time (min)	End time (min)	Resol. USP	Symmetry
1	14.959	12678.221	99.600	14.588	15.854		0.58097
2	17.185	50.959	0.400	16.626	17.865	3.55042	1.01535

Compound 2v



White solid, 52% yield, >99% ee, mp = 43-44 ºC, α_D^{25}= -78 (*c* 0.10, $CHCl_3$).

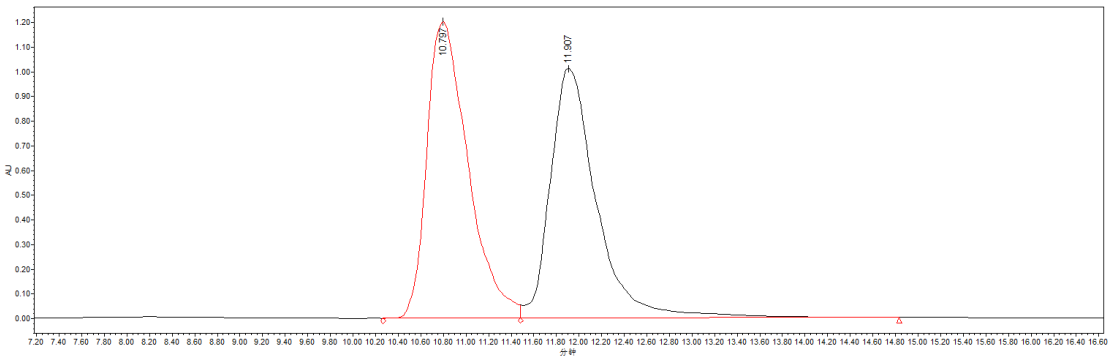
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.05 – 7.03 (m, 1H), 3.42 – 3.38 (m, 1H), 3.01 – 2.93 (m, 1H), 2.71 – 2.66 (m, 4H), 1.64 (s, 9H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.11, 158.96, 142.48, 141.48, 132.44, 129.16, 123.62, 119.38, 89.23, 80.94, 42.07, 28.39, 25.09, 24.67, 23.32.

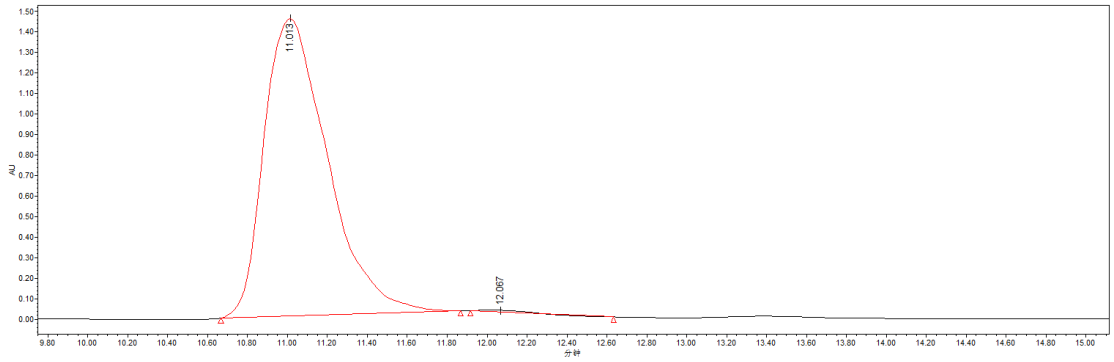
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.93.

HRMS (ESI^+, m/z): calcd for $C_{21}H_{31}BNO_5$ $[M+H]^+$: 388.2289, found: 388.2300.

HPLC analysis: Daicel Chiralpak IA column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 ºC, detection at 254 nm. Retention time (min):11.013 (major) and 12.067 (minor).

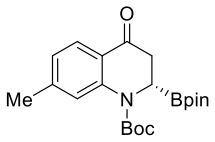


Peak ID	Ret. time	Height	Area	Area%
1	10.797	1199792	30338195	51.41
2	11.907	1012212	28677254	48.59
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	11.013	1451181	32012941	99.52
2	12.067	8187	154329	0.48
Total				100.00

Compound 2w



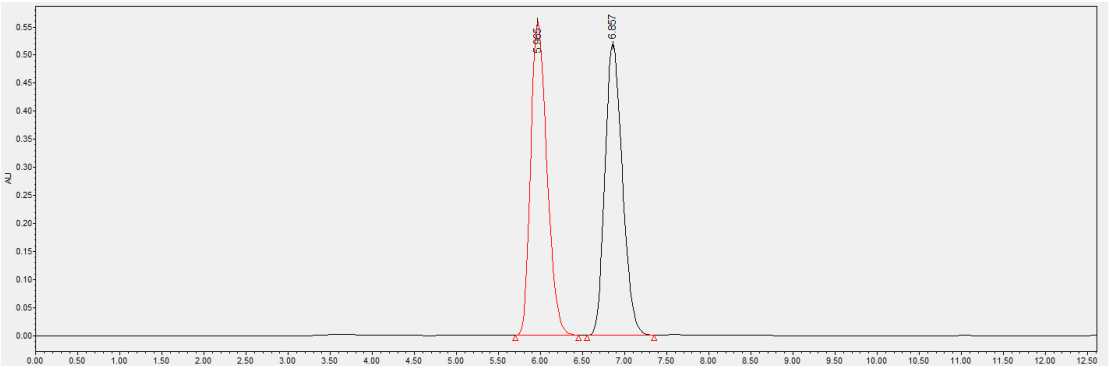
White solid, 81% yield, >99% ee, mp = 121-122 °C, α_D^{25}= -55 (*c* 0.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 3.42 (dd, *J* = 14.9, 3.4 Hz, 1H), 2.92 (dd, *J* = 17.7, 15.0 Hz, 1H), 2.65 (dd, *J* = 17.7, 3.6 Hz, 1H), 2.37 (s, 3H), 1.66 (s, 9H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.91, 159.10, 145.20, 140.29, 128.02, 125.87, 122.32, 120.91, 89.73, 80.90, 39.93, 28.39, 25.10, 24.74, 22.19.

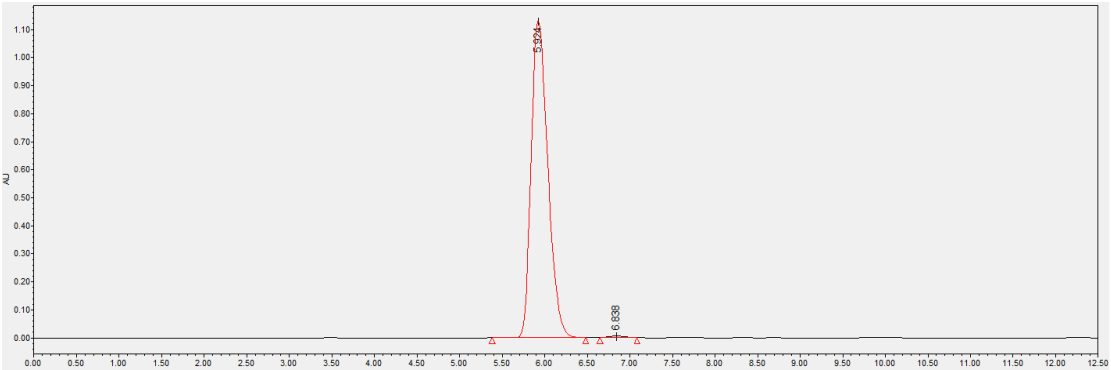
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.45.

HRMS (ESI^+, m/z): calcd for $C_{21}H_{31}BNO_5$ ($[M+H]^+$): 388.2289, found: 388.2290.

HPLC analysis: Daicel Chiralpak ADH column, hexane/iPrOH = 95:5, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 5.924 (major) and 6.838 (minor).

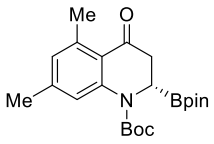


Peak ID	Ret. time	Height	Area	Area%
1	5.965	558209	7515280	50.19
2	6.857	519690	7457645	49.81
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	5.924	1131845	15391665	99.52
2	6.838	5771	74863	0.48
Total				100.00

Compound 2x



White solid, 80% yield, 98% ee, mp = 105-106 °C, α_D^{25}= -93 (*c* 0.10, $CHCl_3$).

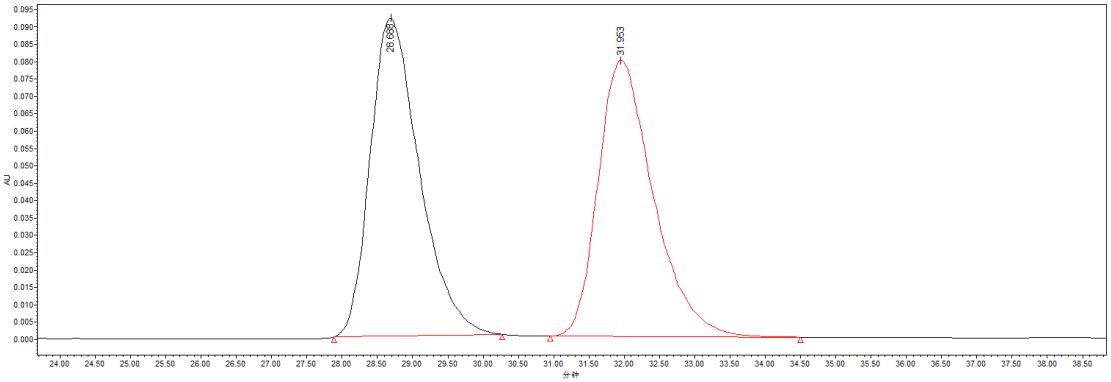
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.83 (s, 1H), 3.35 (dd, *J* = 14.6, 3.7 Hz, 1H), 2.91 (dd, *J* = 17.8, 14.6 Hz, 1H), 2.65 – 2.60 (m, 4H), 2.30 (s, 3H), 1.62 (s, 9H), 1.21 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.83, 158.98, 143.29, 142.43, 141.42, 130.11, 121.28, 119.85, 89.14, 80.87, 41.94, 28.39, 25.10, 24.69, 23.30, 21.82.

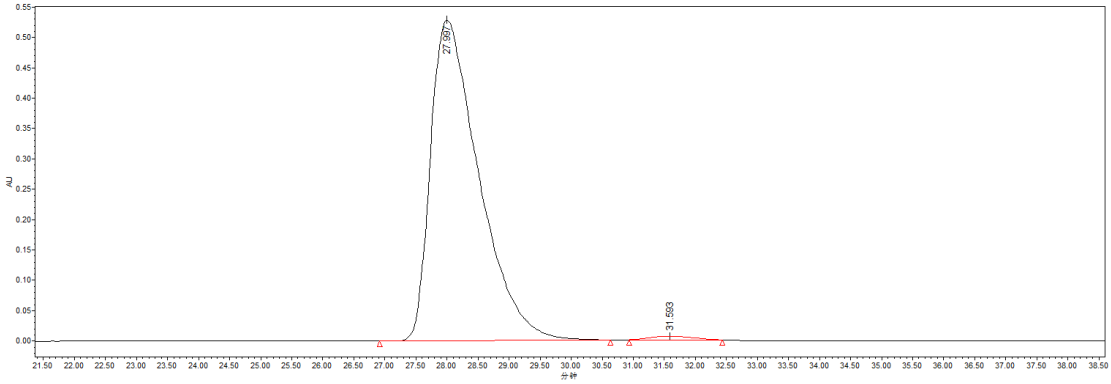
^{11}B NMR (128 MHz, $CDCl_3$) δ 15.57.

HRMS (ESI^+, m/z): calcd for $C_{22}H_{33}BNO_5$ $[M+H]^+$: 402.2446, found: 402.2442.

HPLC analysis: Daicel Chiralpak IC column, hexane/iPrOH = 97:3, flow rate = 1.0 mL/min, 25 °C, detection at 254 nm. Retention time (min): 27.997 (major) and 31.593 (minor).

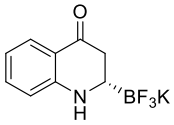


Peak ID	Ret. time	Height	Area	Area%
1	28.688	91499	4437304	50.57
2	31.953	79484	4336691	49.43
Total				100.00



Peak ID	Ret. time	Height	Area	Area%
1	27.997	527866	28541049	99.01
2	31.593	6087	284005	0.99
Total				100.00

Compound 3a



White solid, 70% yield, mp = 240-241 °C, α_D^{25}= - 63 (*c* 0.10, H_2O).

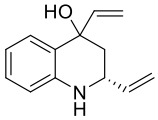
^{1}H NMR (400 MHz, D_2O) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.84 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.20 – 7.08 (m, 1H), 3.31 – 3.19 (m, 1H), 2.70 (dd, *J* = 17.4, 15.4 Hz, 1H), 2.54 (dd, *J* = 17.4, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, D_2O) δ 200.23, 142.89, 135.58, 127.15, 123.17, 122.47, 119.67, 38.39.

^{11}B NMR (128 MHz, D_2O) δ 5.92.

HRMS (ESI$^+$, m/z): calcd for $C_9H_8BF_3KNONa$ ([M+Na]$^+$): 276.0180, found: 276.0164.

Compound 3b



Colorless oil, 70% yield, α_D^{25}= -7 (*c* 0.10, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 1H), 7.36 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.19 (td, *J* = 7.7, 1.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.91 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.83 – 5.69 (m, 1H), 5.14 – 4.95 (m, 4H), 4.80 (q, *J* = 7.2 Hz, 1H), 2.35 (dd, *J* = 13.3, 7.1 Hz, 1H), 1.87 (dd, *J* = 13.3, 8.0 Hz, 1H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.62, 139.85, 136.97, 134.80, 134.01, 126.47, 124.67, 123.97, 123.17, 114.15, 113.74, 70.98, 52.31, 42.89, 27.27.

HRMS (ESI$^+$, m/z): calcd for $C_{18}H_{23}NO_3Na$ ([M+Na]$^+$): 324.1570, found: 324.1562.

7. X-ray crystal structure of compound 2m (CCDC: 2116198. Crystal structure with thermal ellipsoids drawn at 50% probability level.**)**

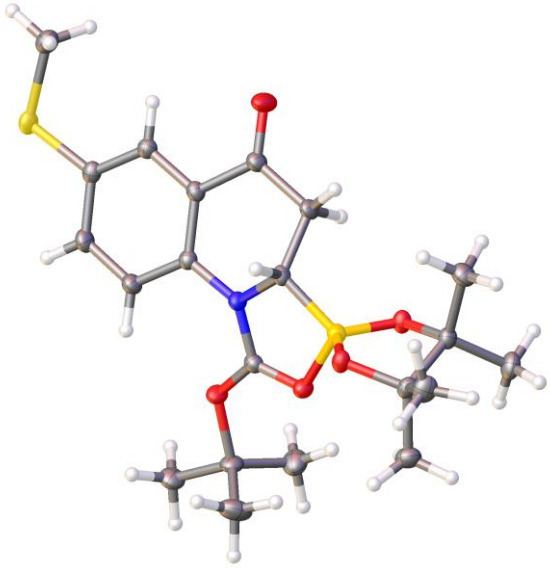


Table 1 Crystal data and structure refinement for 2m.

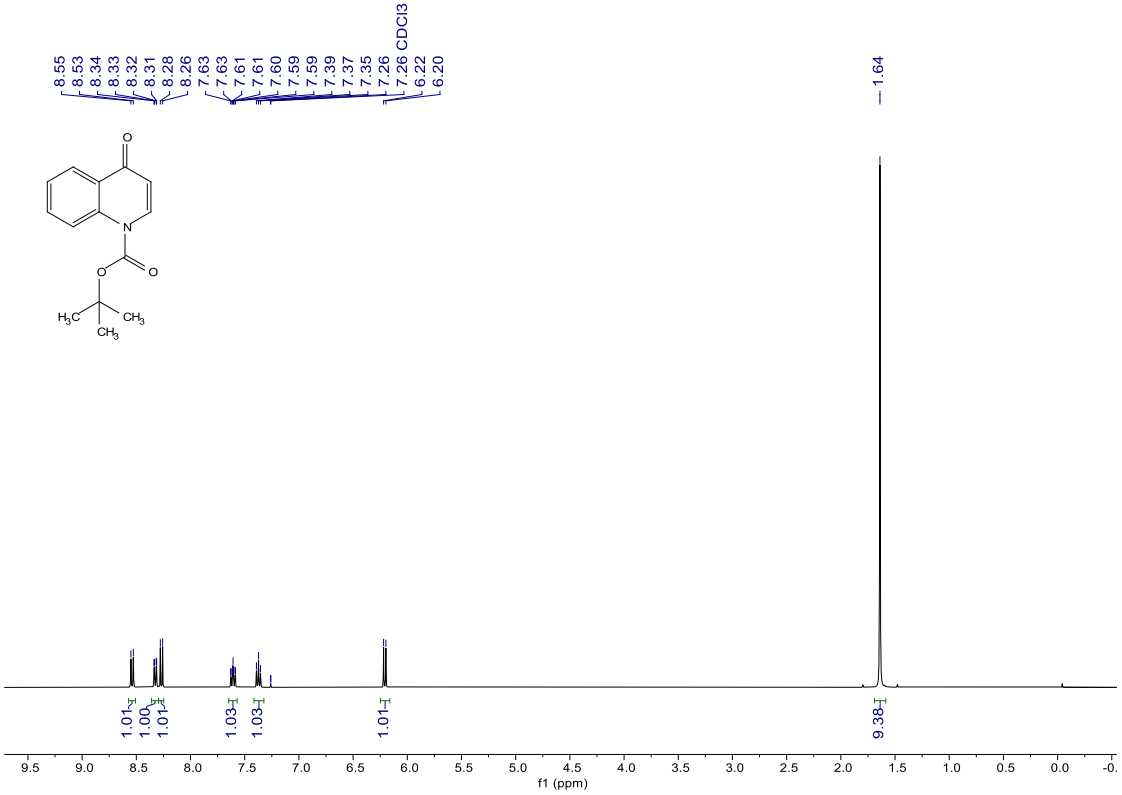
Empirical formula	$C_{21}H_{32}BNO_6S$
Formula weight	437.34
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.2610(2)
b/Å	16.8304(6)
c/Å	18.6890(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2283.90(13)
Z	4
ρ_{calc}g/cm^3	1.272
μ/mm^{-1}	1.562
F(000)	936.0
Crystal size/mm^3	0.26 × 0.23 × 0.21
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.068 to 148.898
Index ranges	$-8 \le h \le 7$, $-20 \le k \le 21$, $-22 \le l \le 23$
Reflections collected	30751

Independent reflections	4594 [R_{int} = 0.0322, R_{sigma} = 0.0207]
Data/restraints/parameters	4594/0/283
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0236, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0239, wR_2 = 0.0596
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.19
Flack parameter	0.029(13)

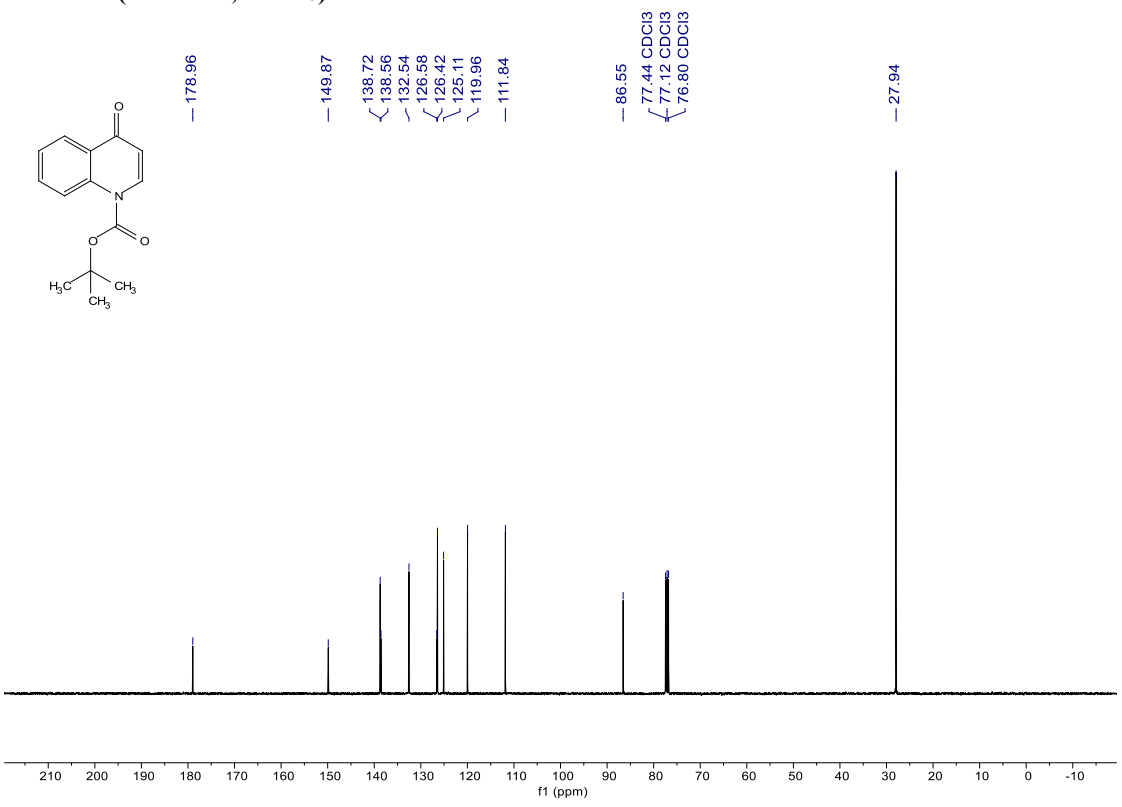
8. NMR spectra of the compounds 1a-2x and 3a-3b

Compound 1a

^{1}H NMR (400 MHz, $CDCl_3$)

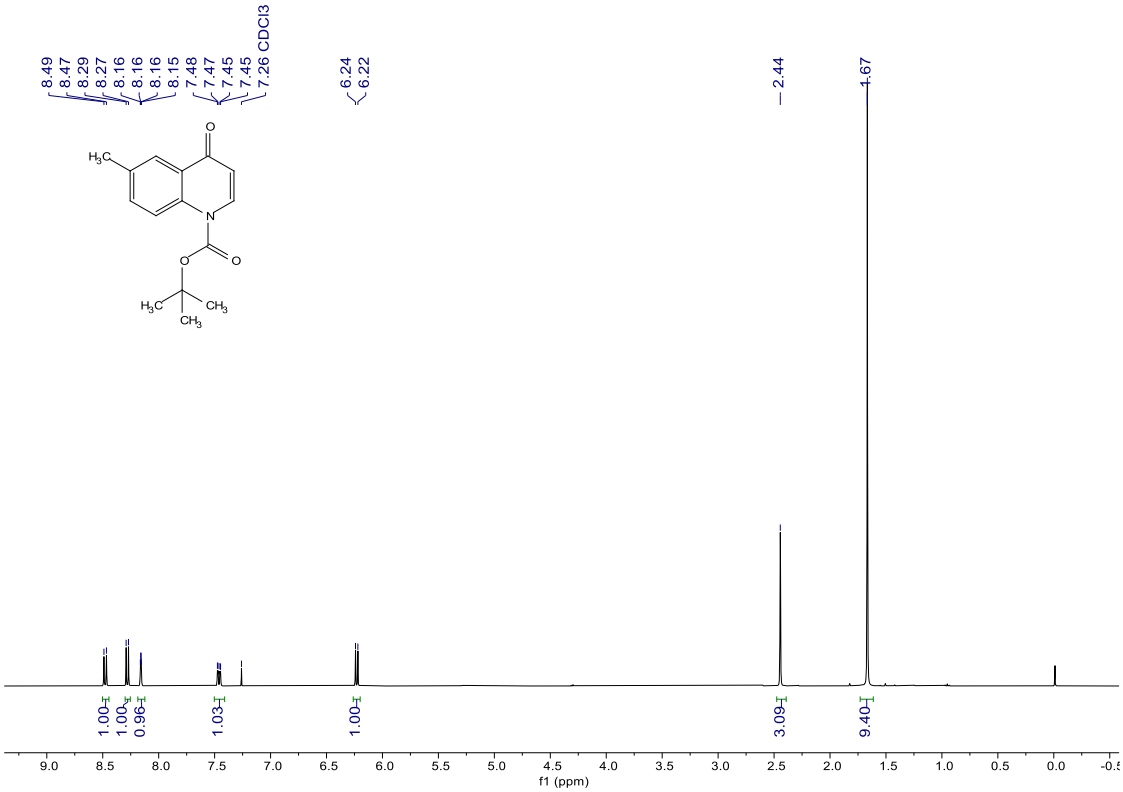


^{13}C NMR (101 MHz, $CDCl_3$)

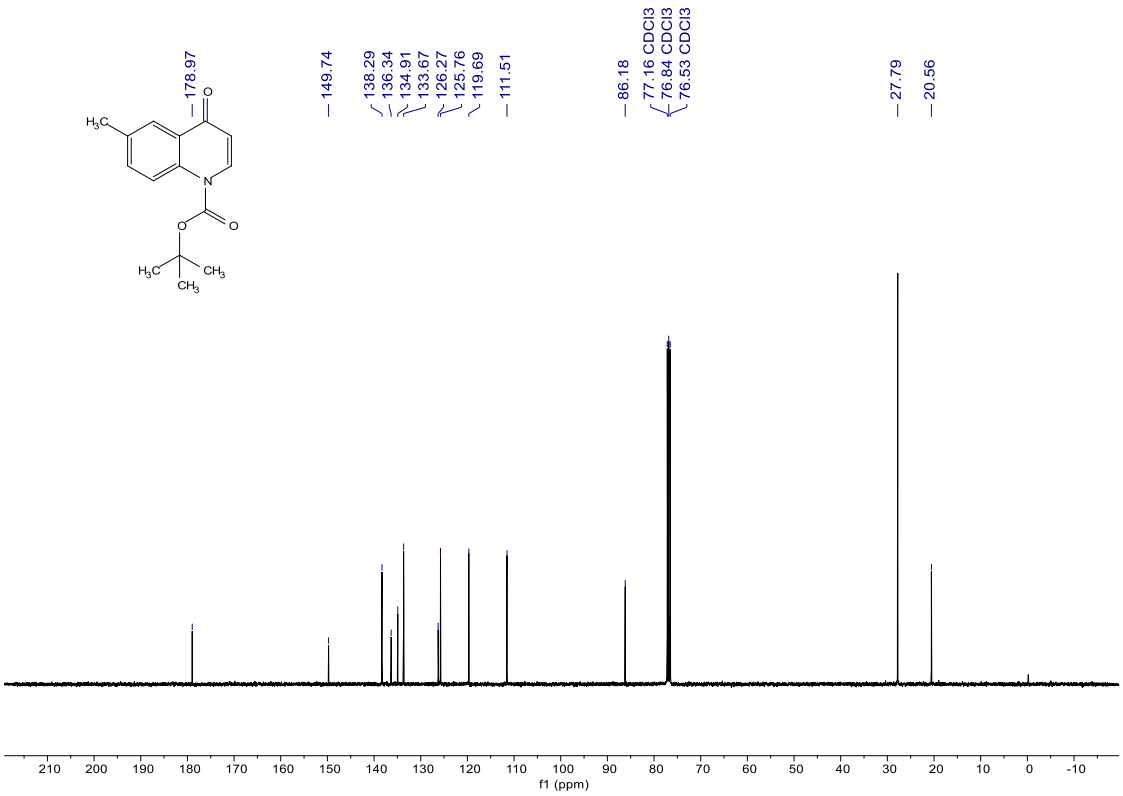


Compound 1b

^{1}H NMR (400 MHz, $CDCl_3$)

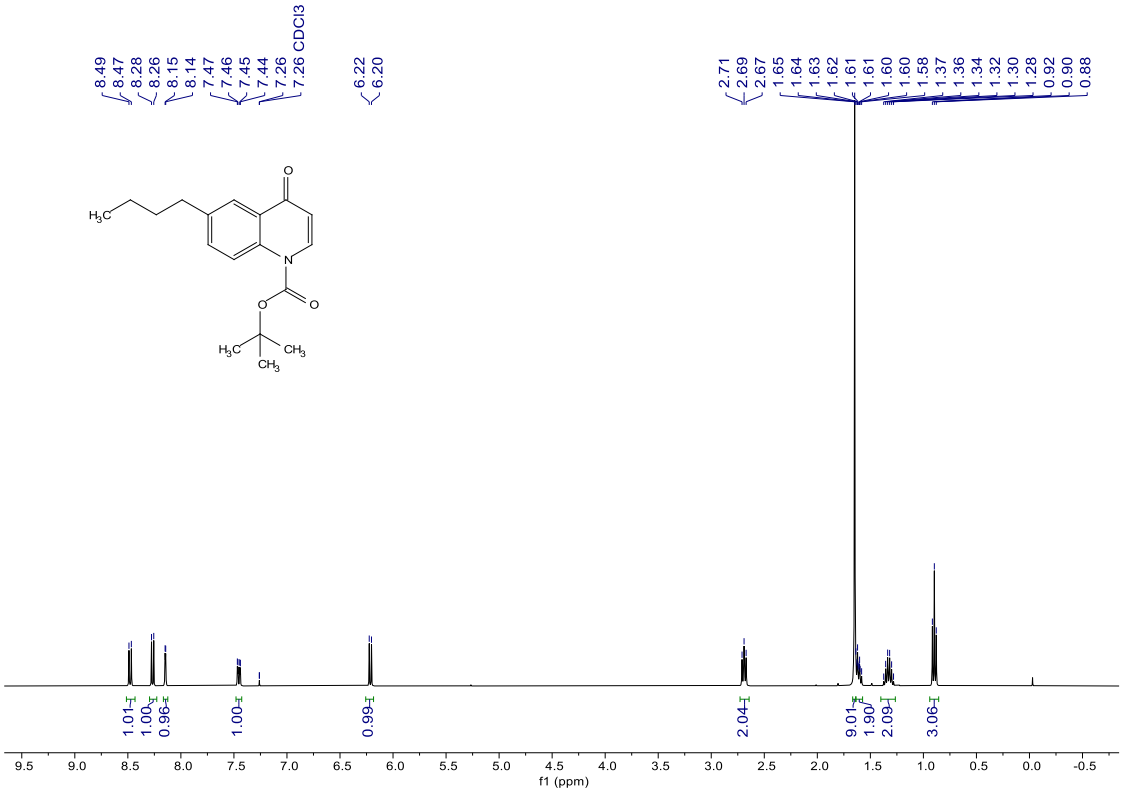


^{13}C NMR (101 MHz, $CDCl_3$)

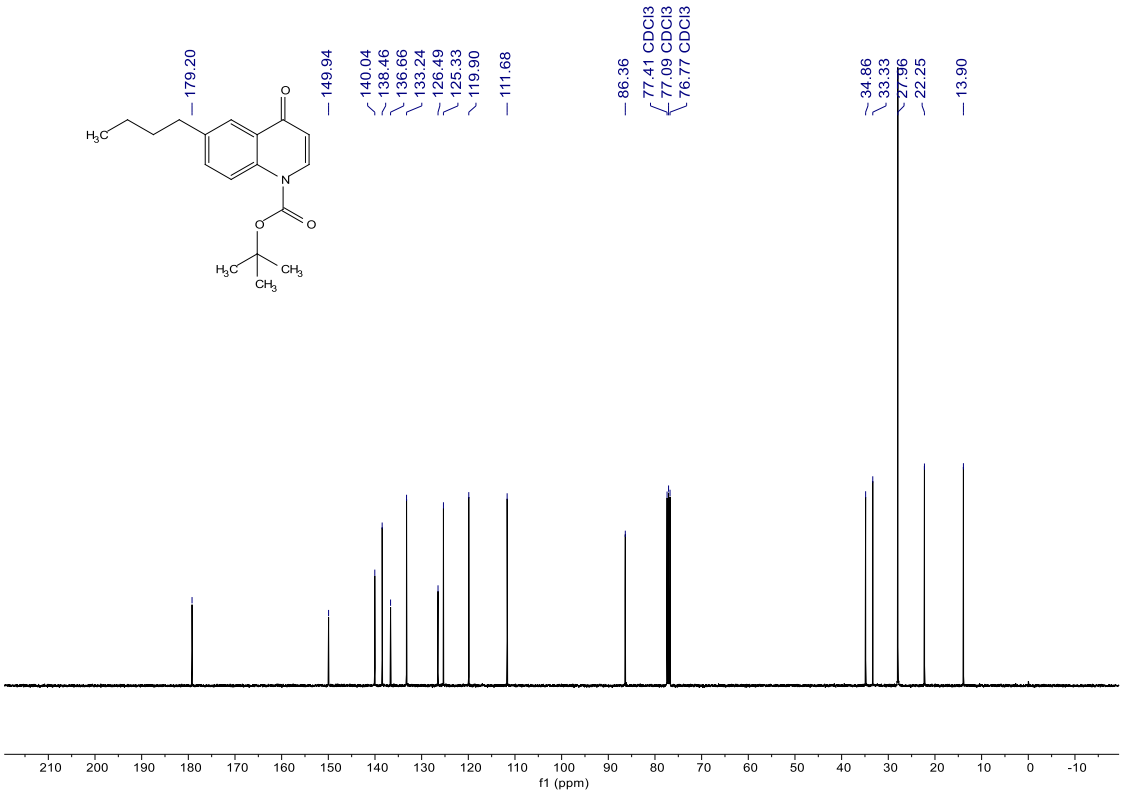


Compound 1c

^{1}H NMR (400 MHz, $CDCl_3$)

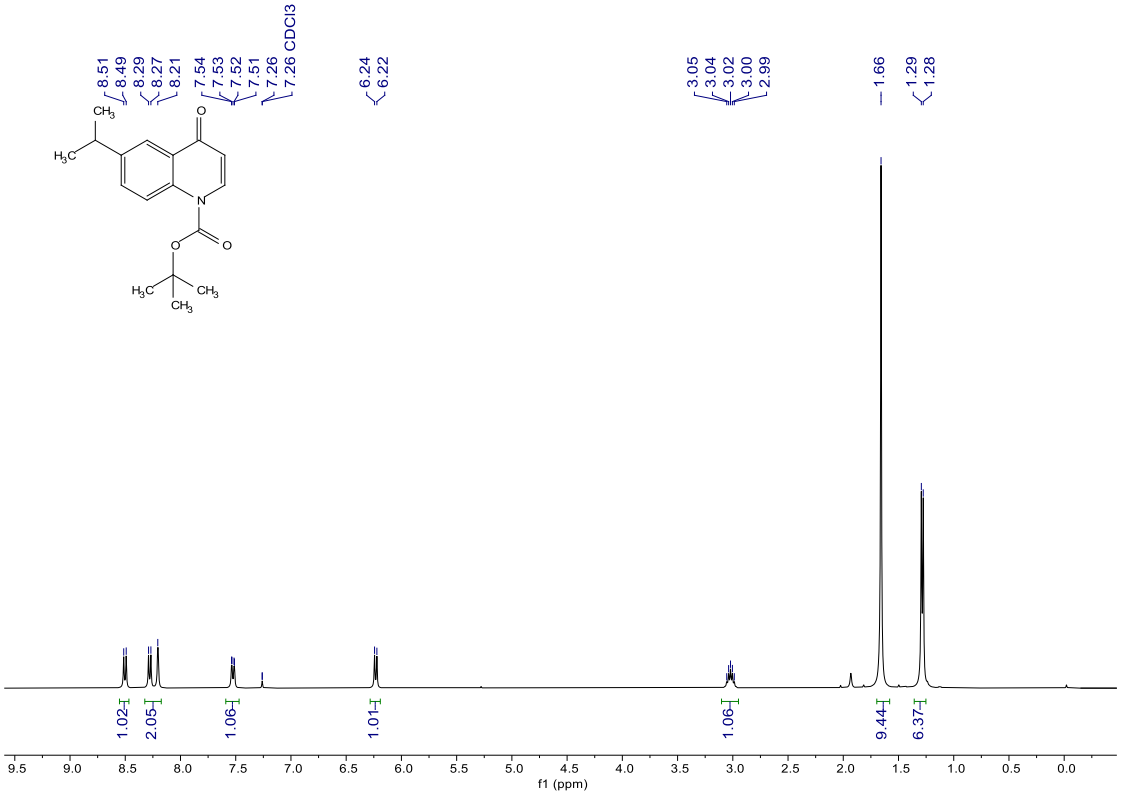


^{13}C NMR (101 MHz, $CDCl_3$)

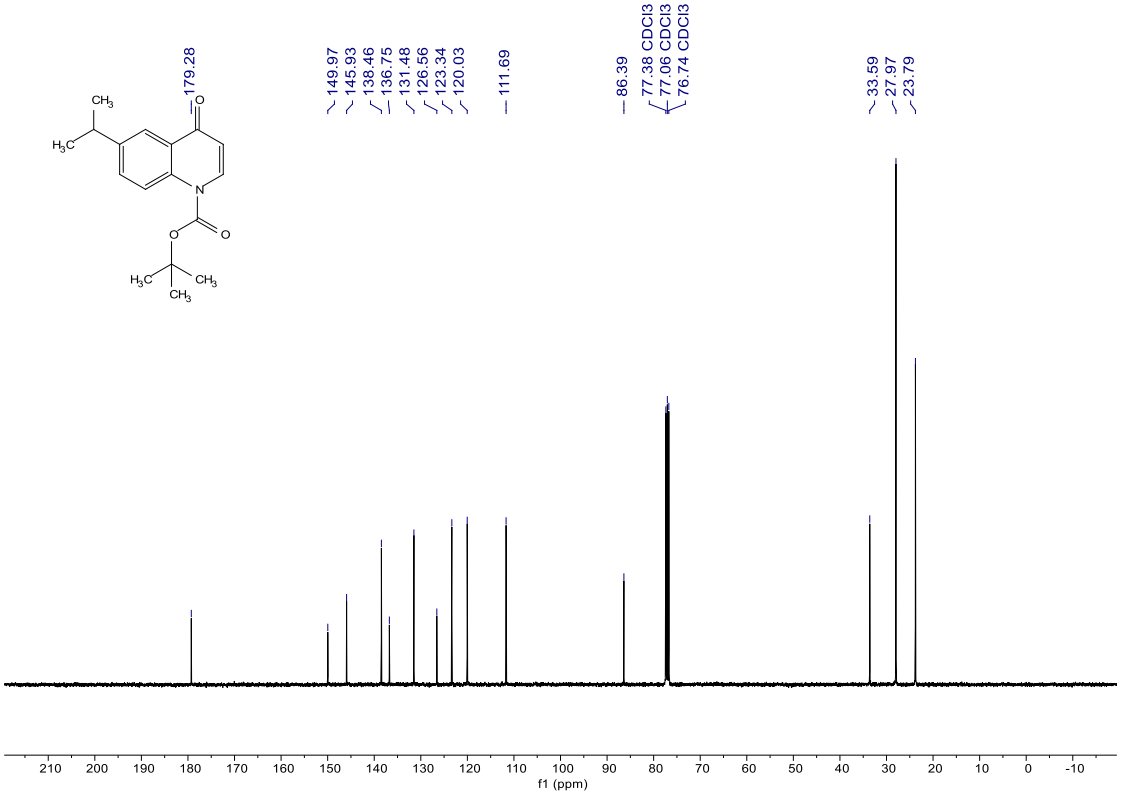


Compound 1d

^{1}H NMR (400 MHz, $CDCl_3$)

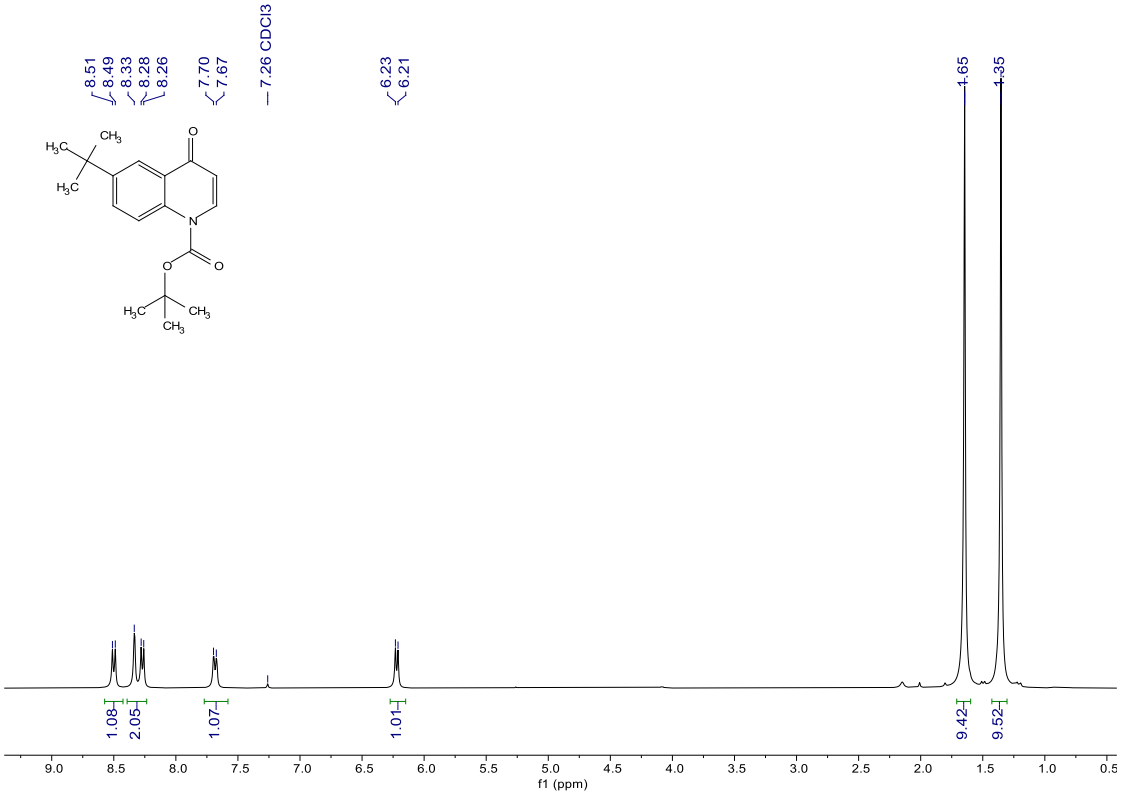


^{13}C NMR (101 MHz, $CDCl_3$)

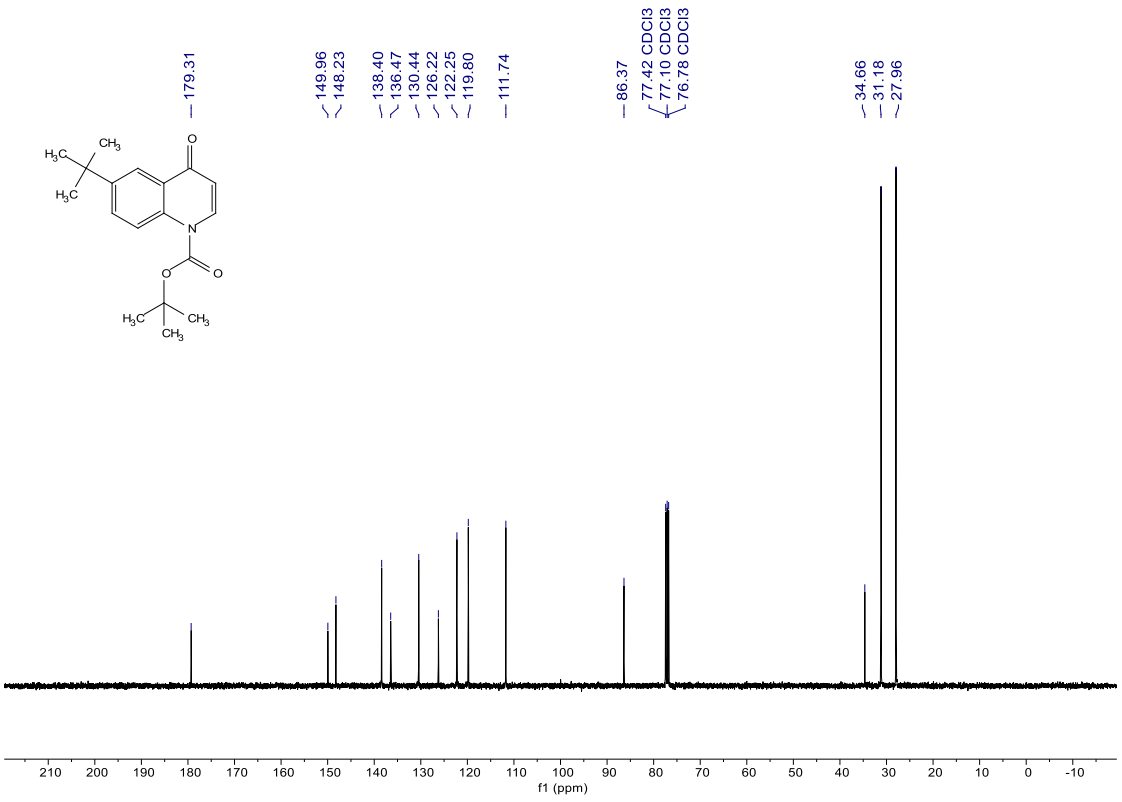


Compound 1e

^{1}H NMR (400 MHz, $CDCl_3$)

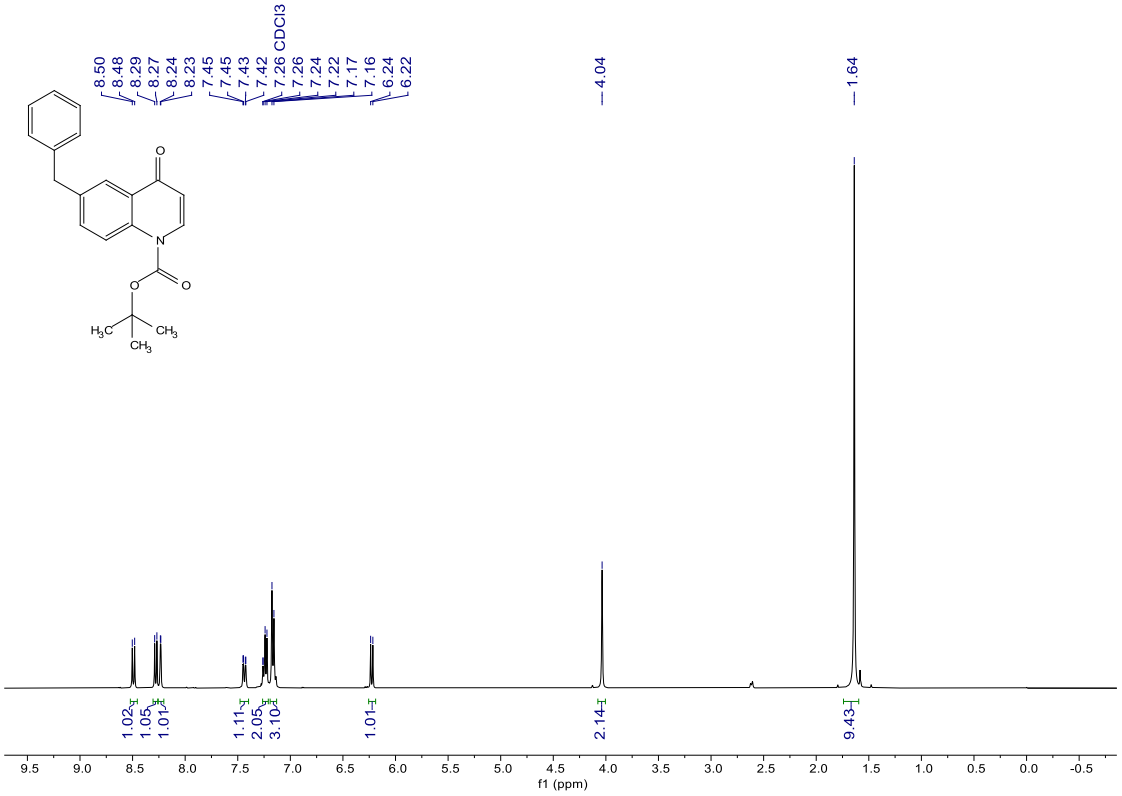


^{13}C NMR (101 MHz, $CDCl_3$)

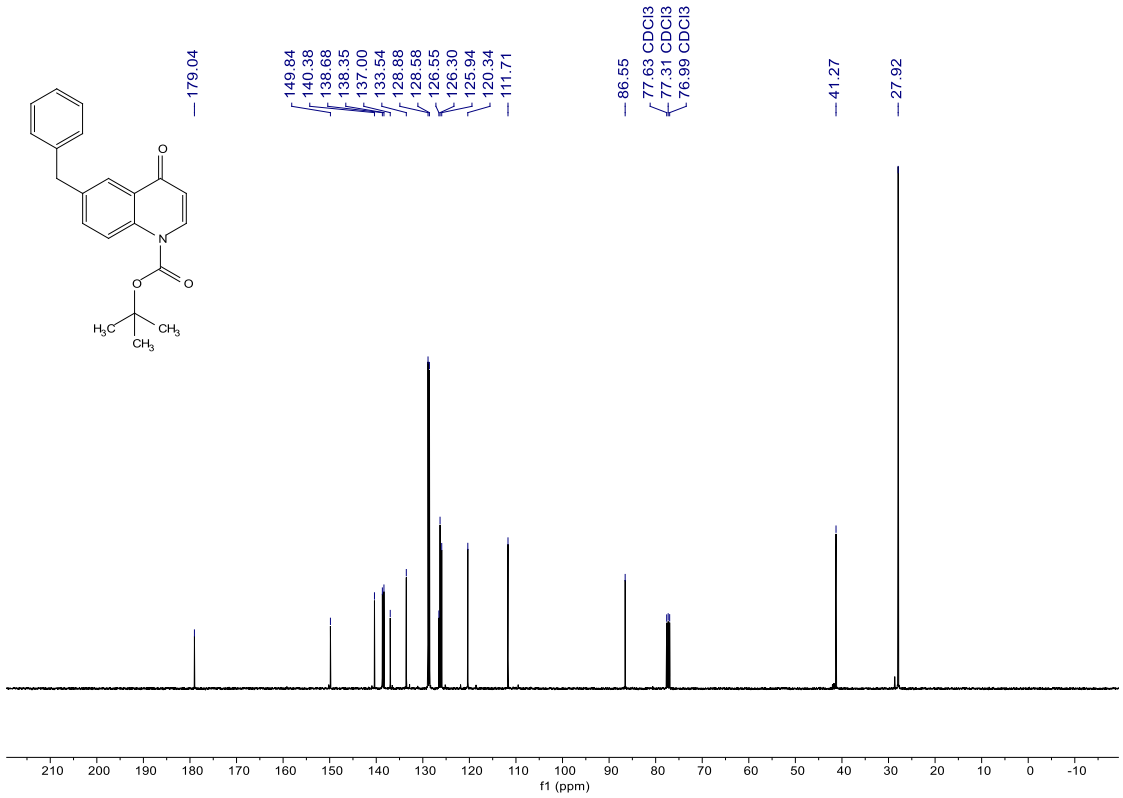


Compound 1f

^{1}H NMR (400 MHz, $CDCl_3$)

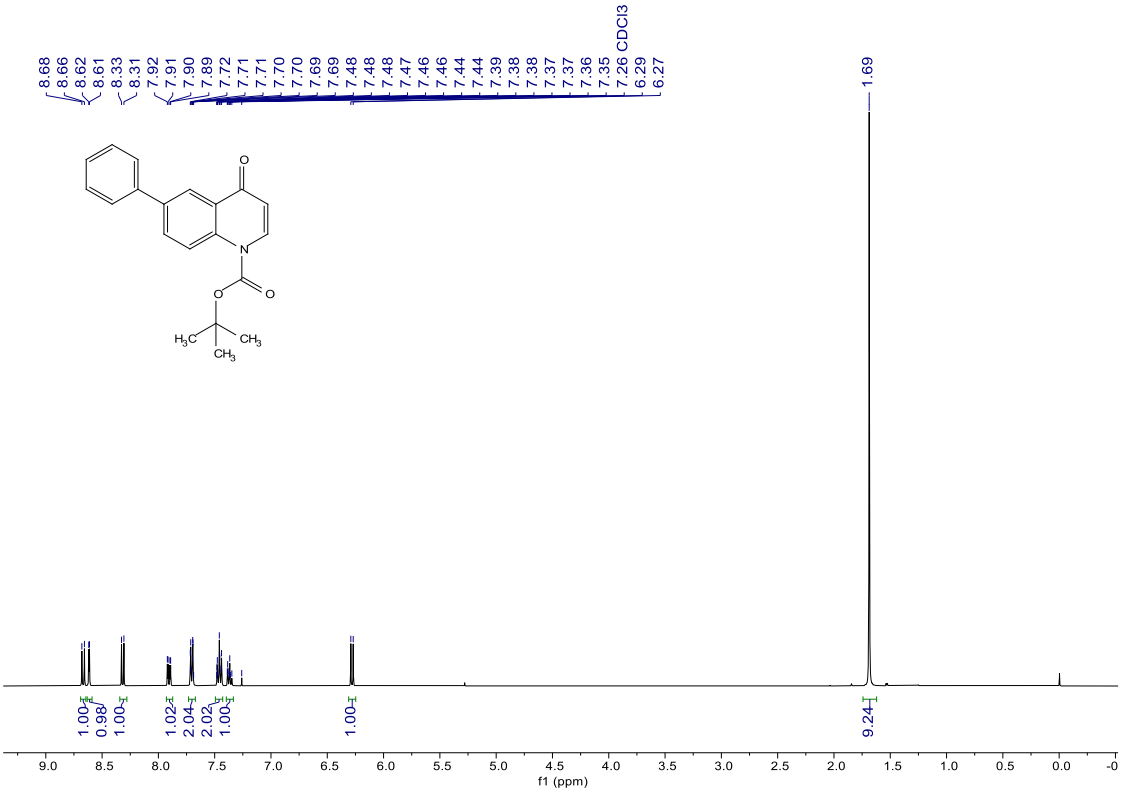


^{13}C NMR (101 MHz, $CDCl_3$)

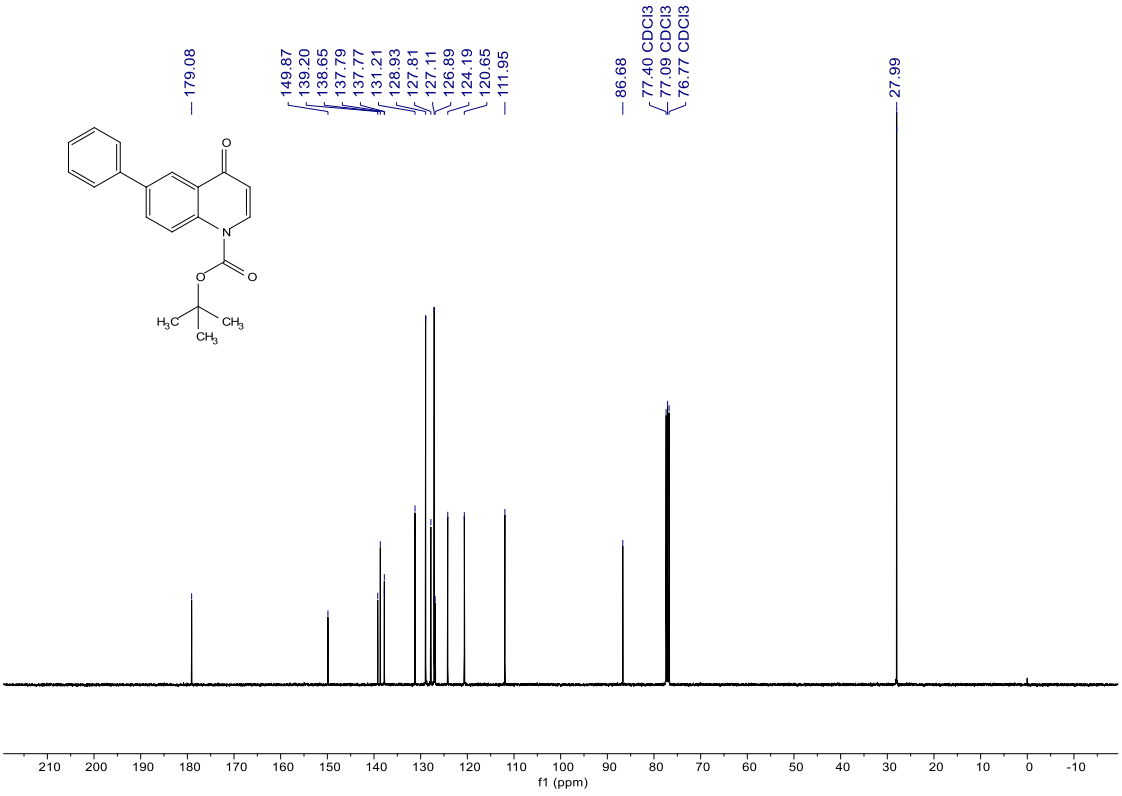


Compound 1g

^{1}H NMR (400 MHz, $CDCl_3$)

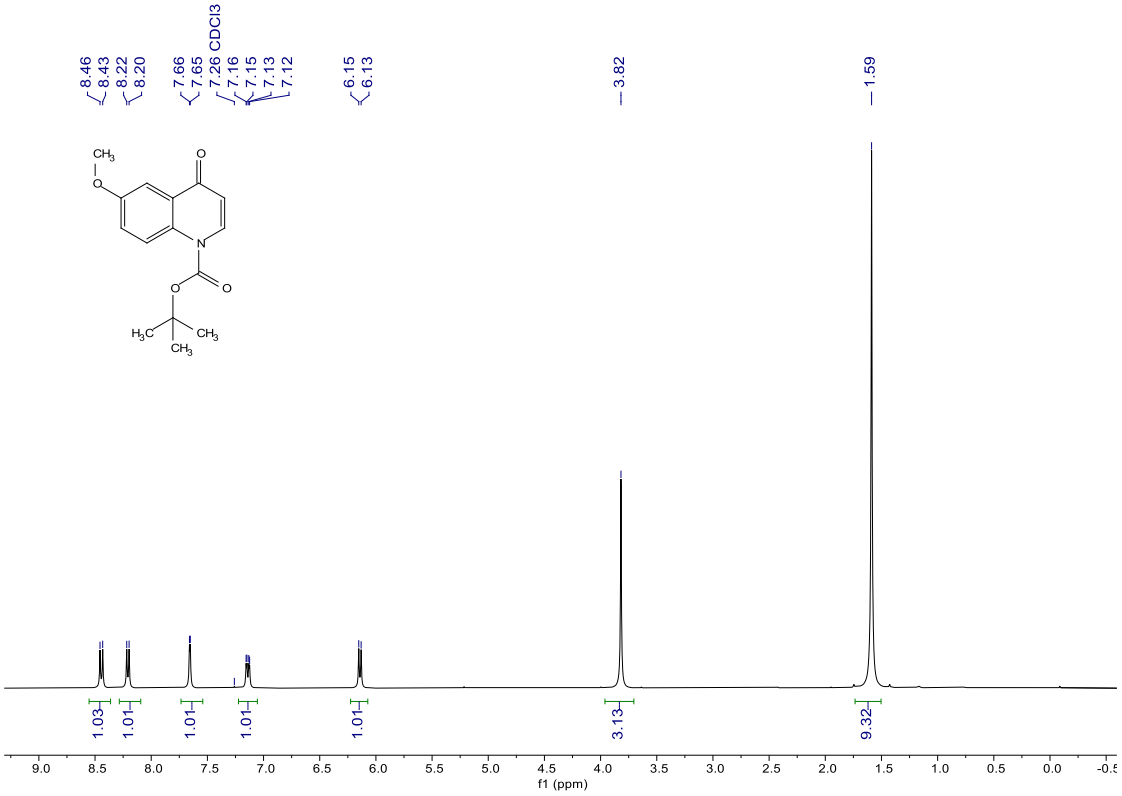


^{13}C NMR (101 MHz, $CDCl_3$)

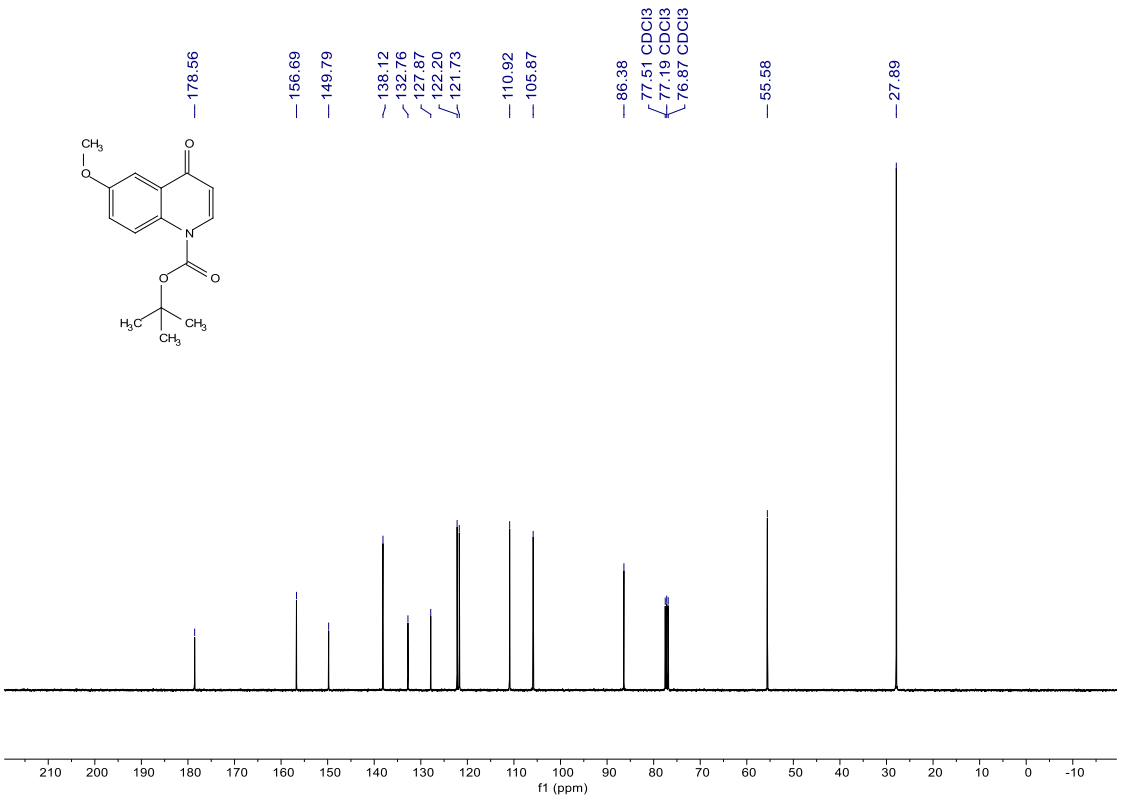


Compound 1h

^{1}H NMR (400 MHz, $CDCl_3$)

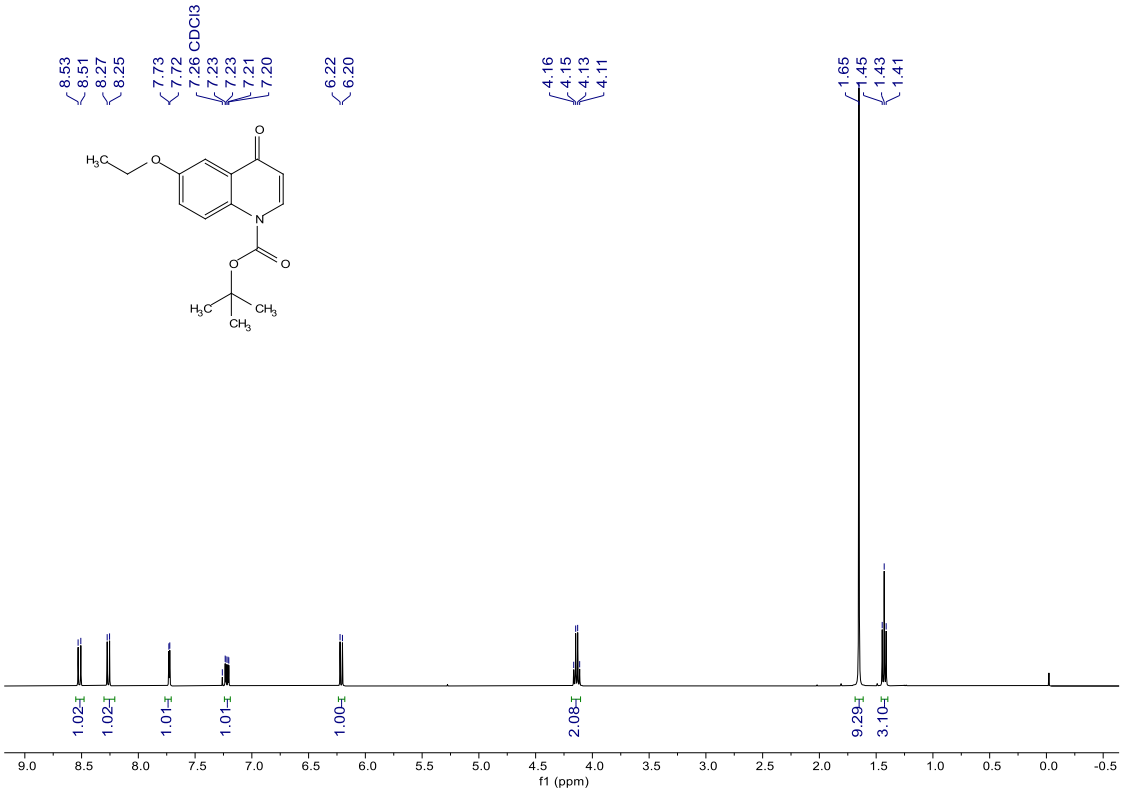


^{13}C NMR (101 MHz, $CDCl_3$)

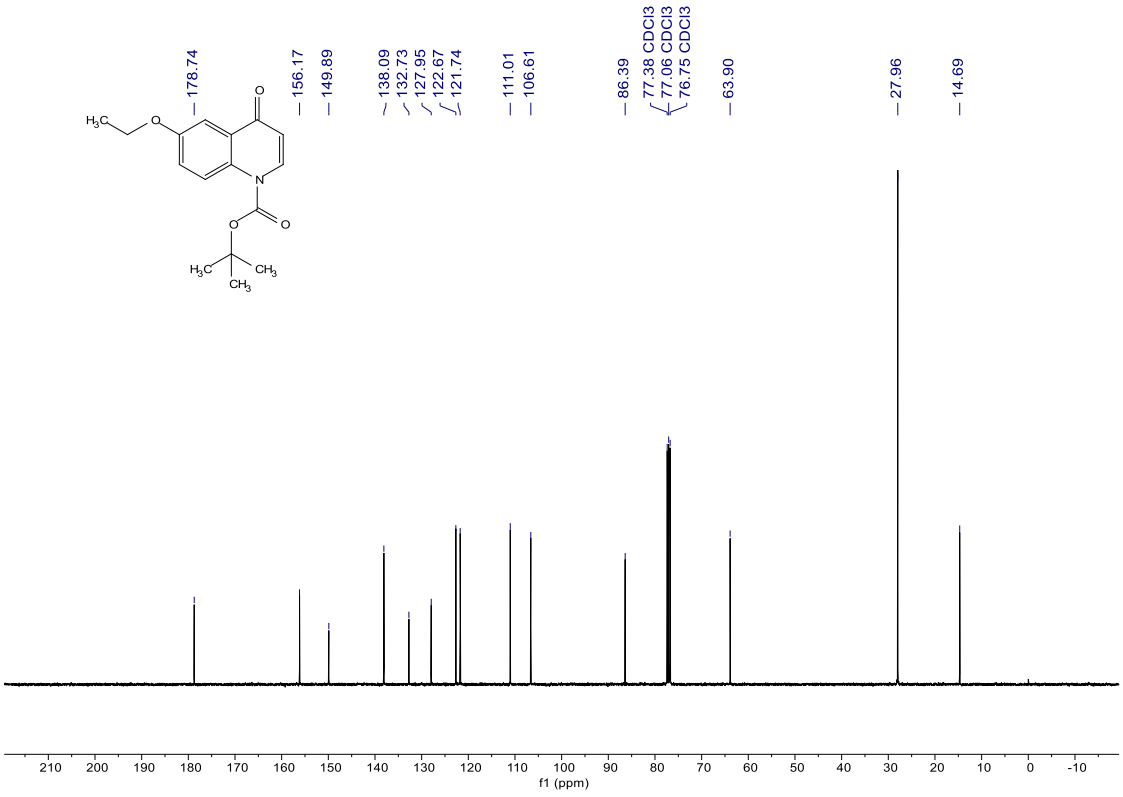


Compound 1i

^{1}H NMR (400 MHz, $CDCl_3$)

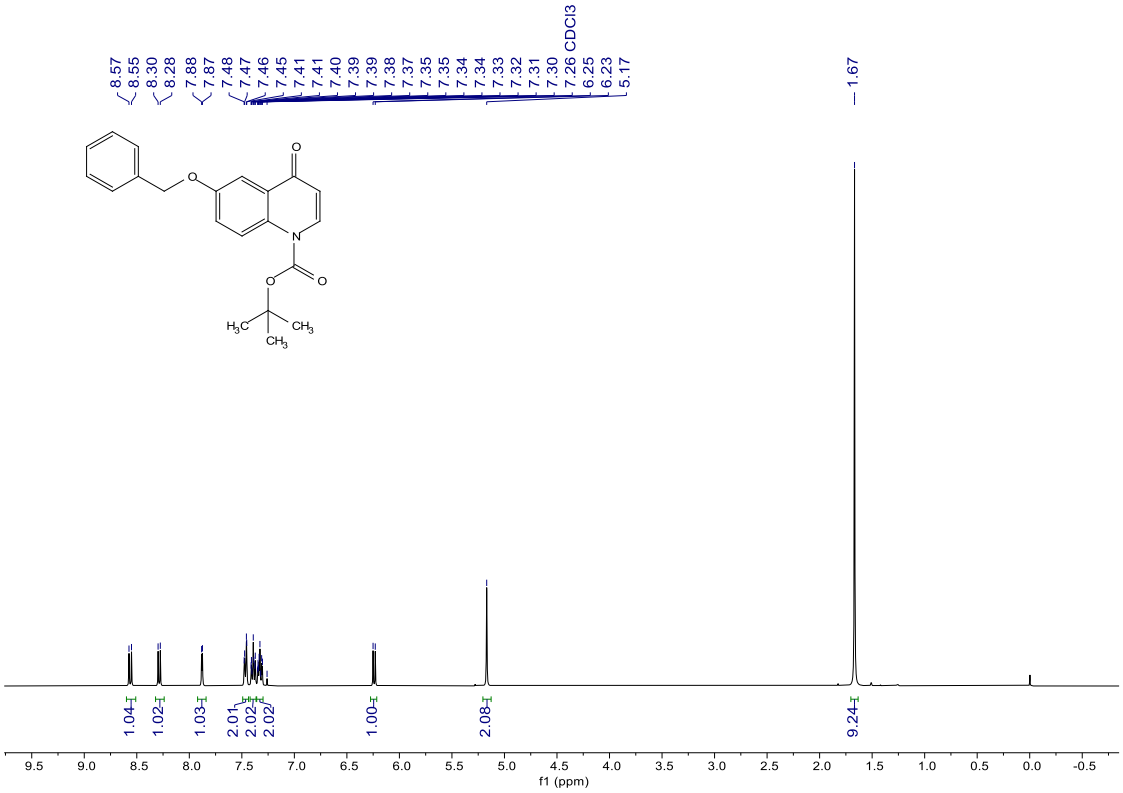


^{13}C NMR (101 MHz, $CDCl_3$)

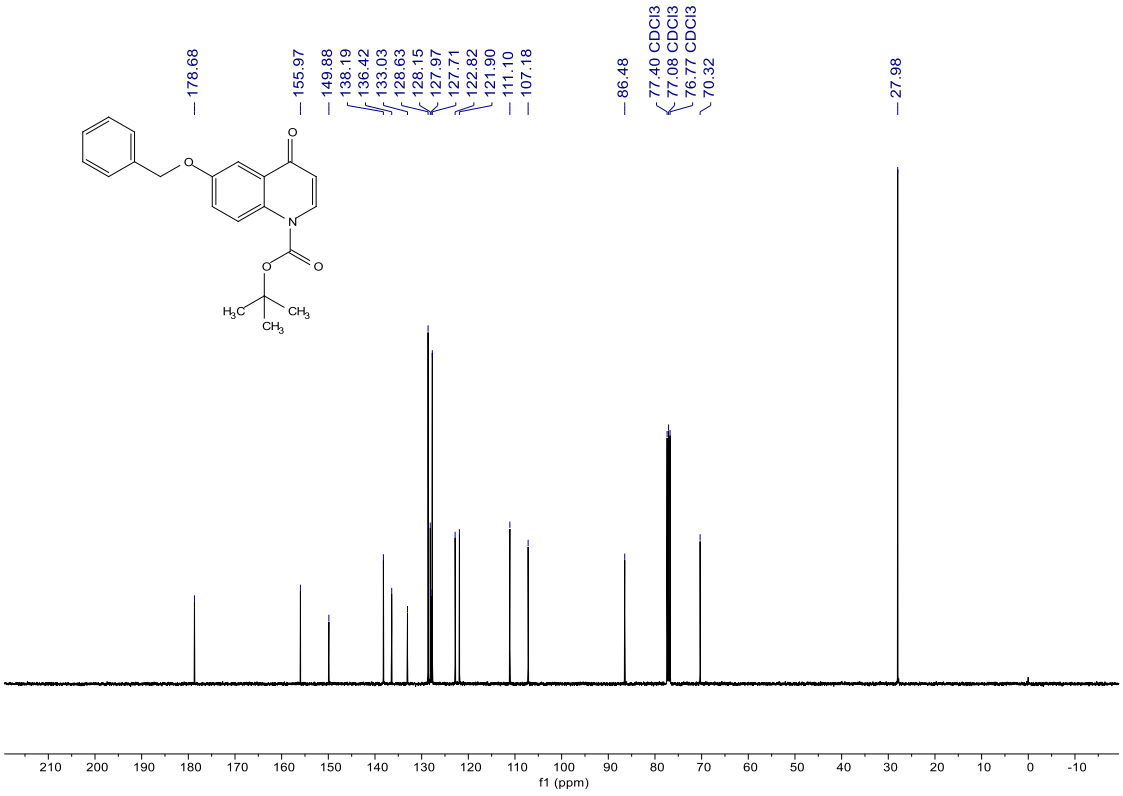


Compound 1j

^{1}H NMR (400 MHz, $CDCl_3$)

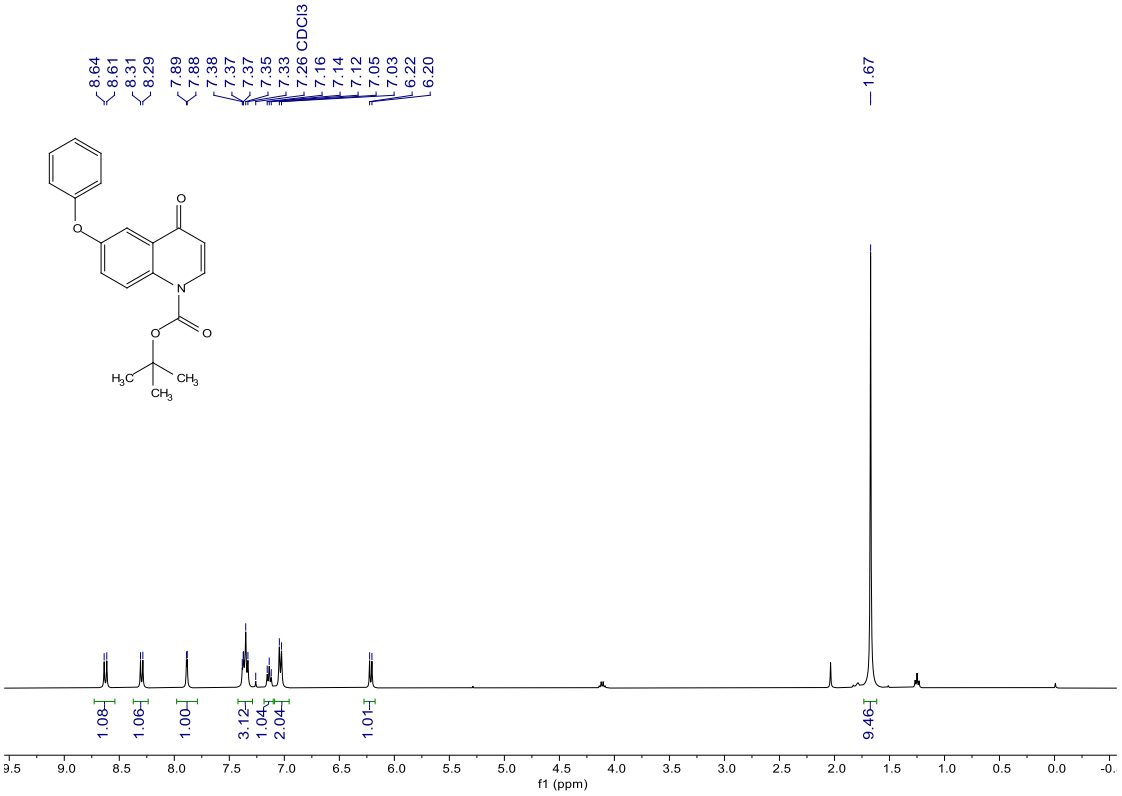


^{13}C NMR (101 MHz, $CDCl_3$)

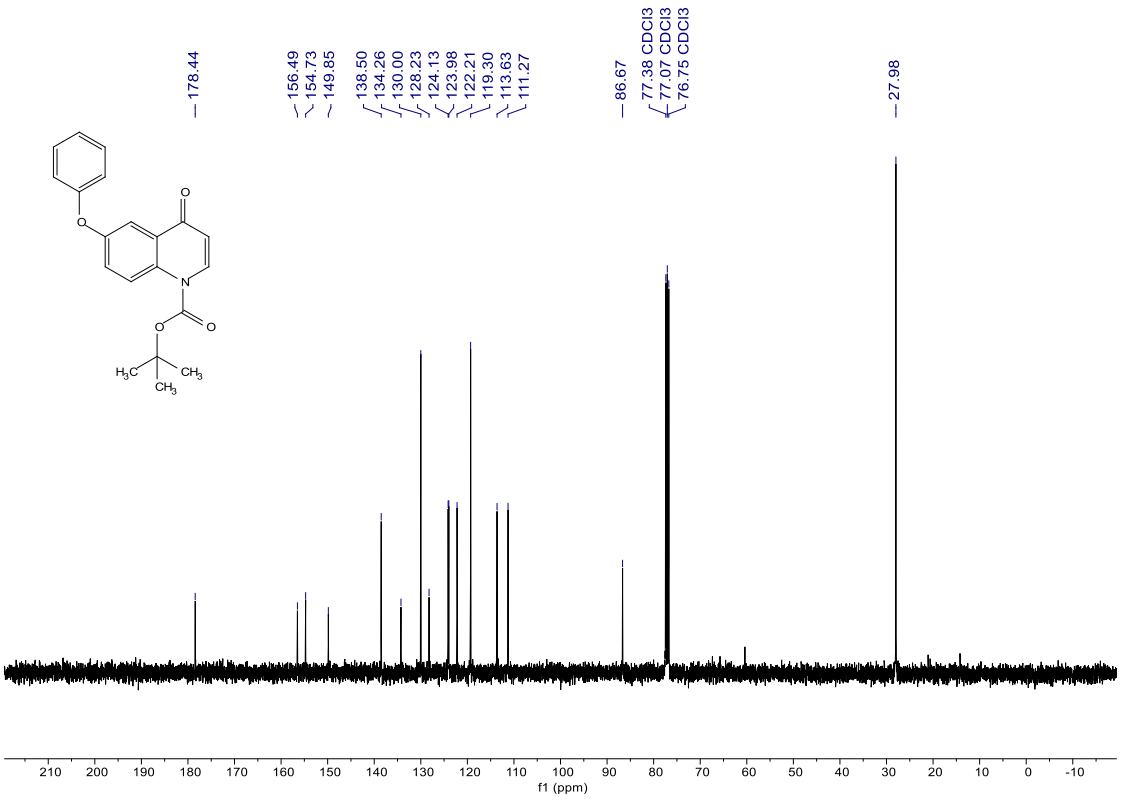


Compound 1k

^{1}H NMR (400 MHz, $CDCl_3$)

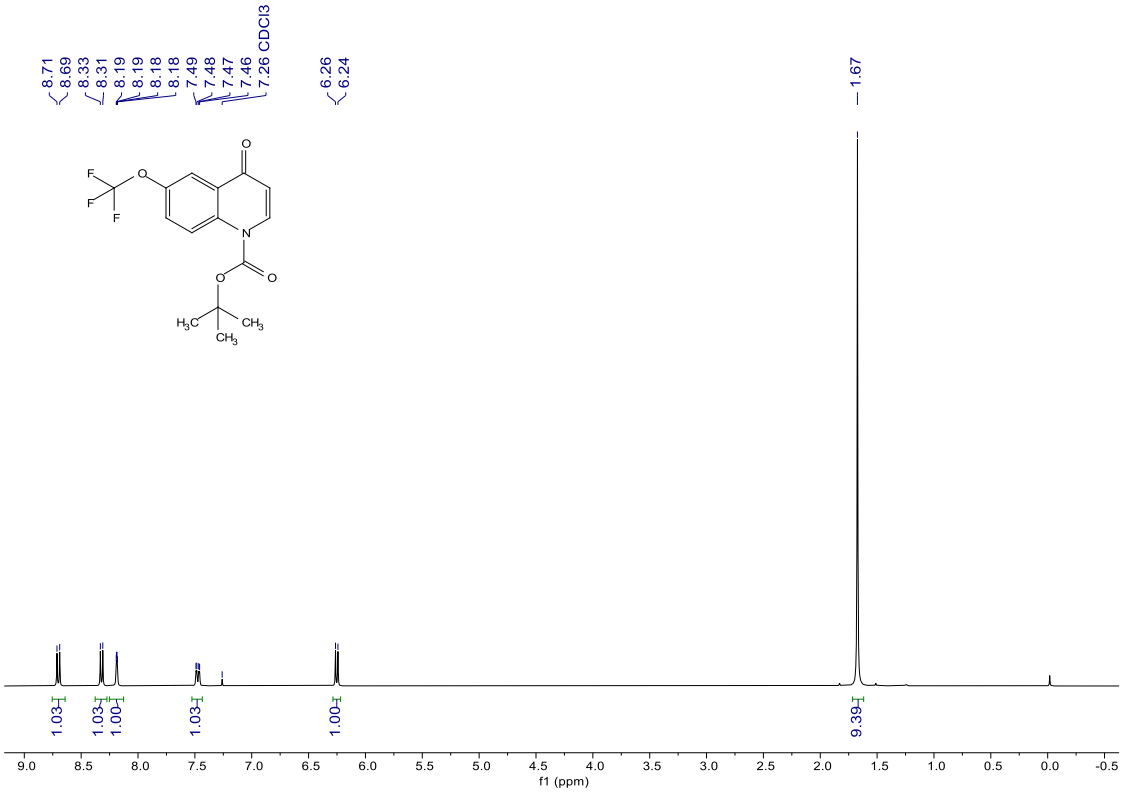


^{13}C NMR (101 MHz, $CDCl_3$)

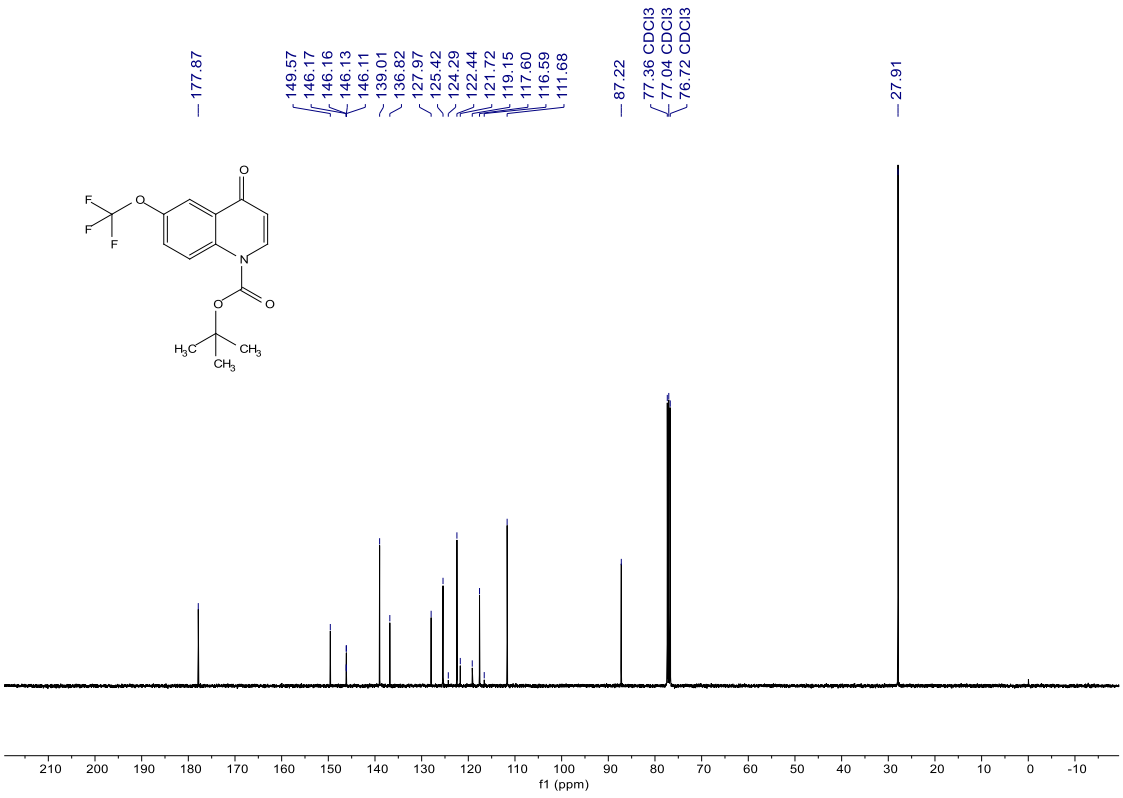


Compound 1l

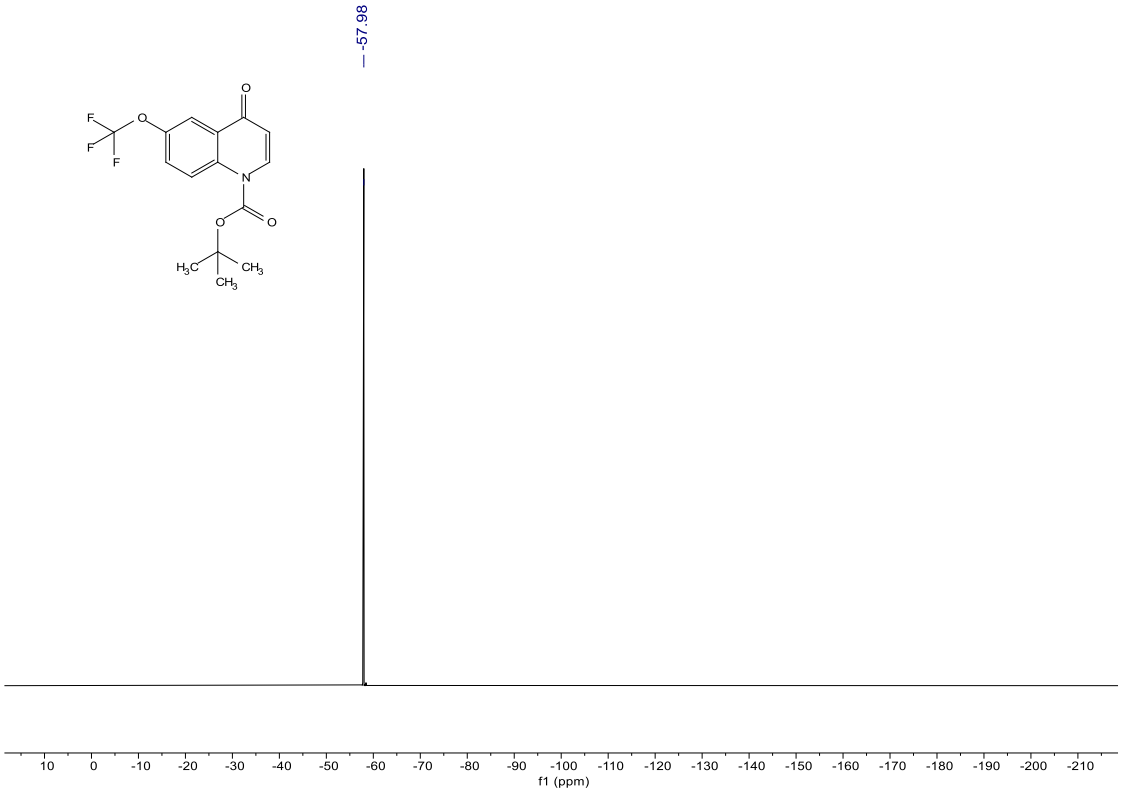
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

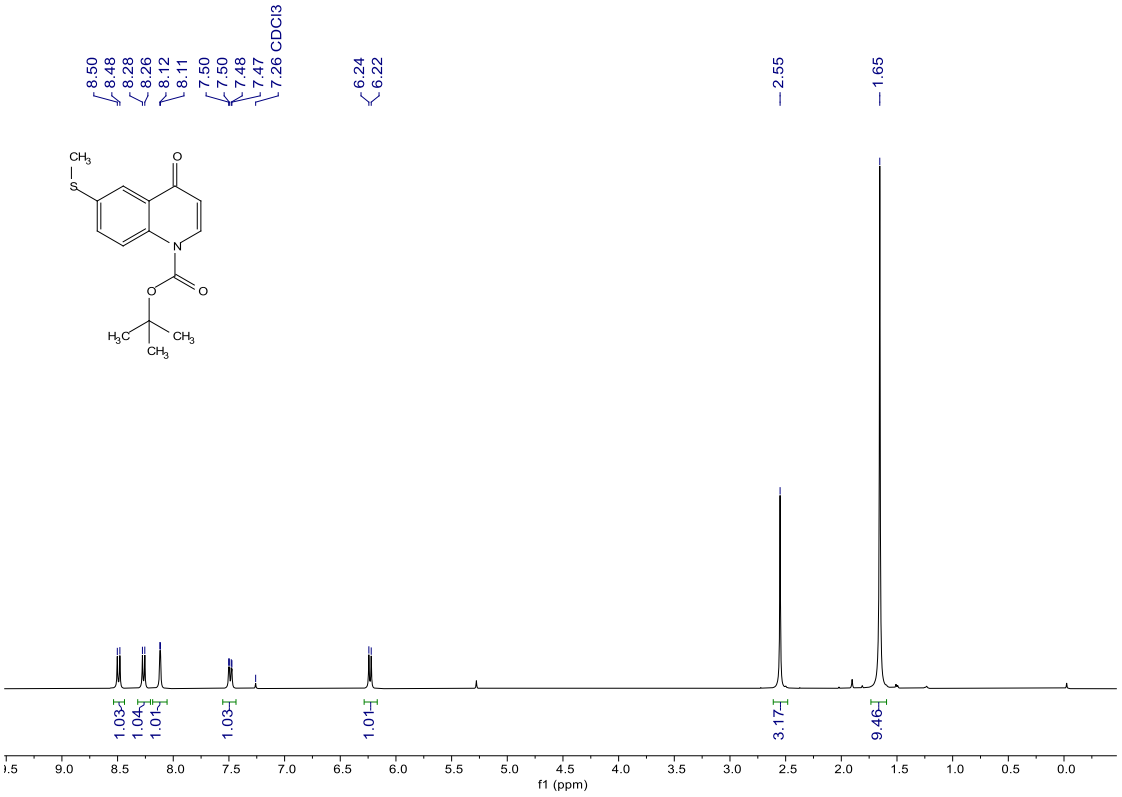


^{19}F NMR (376 MHz, $CDCl_3$)

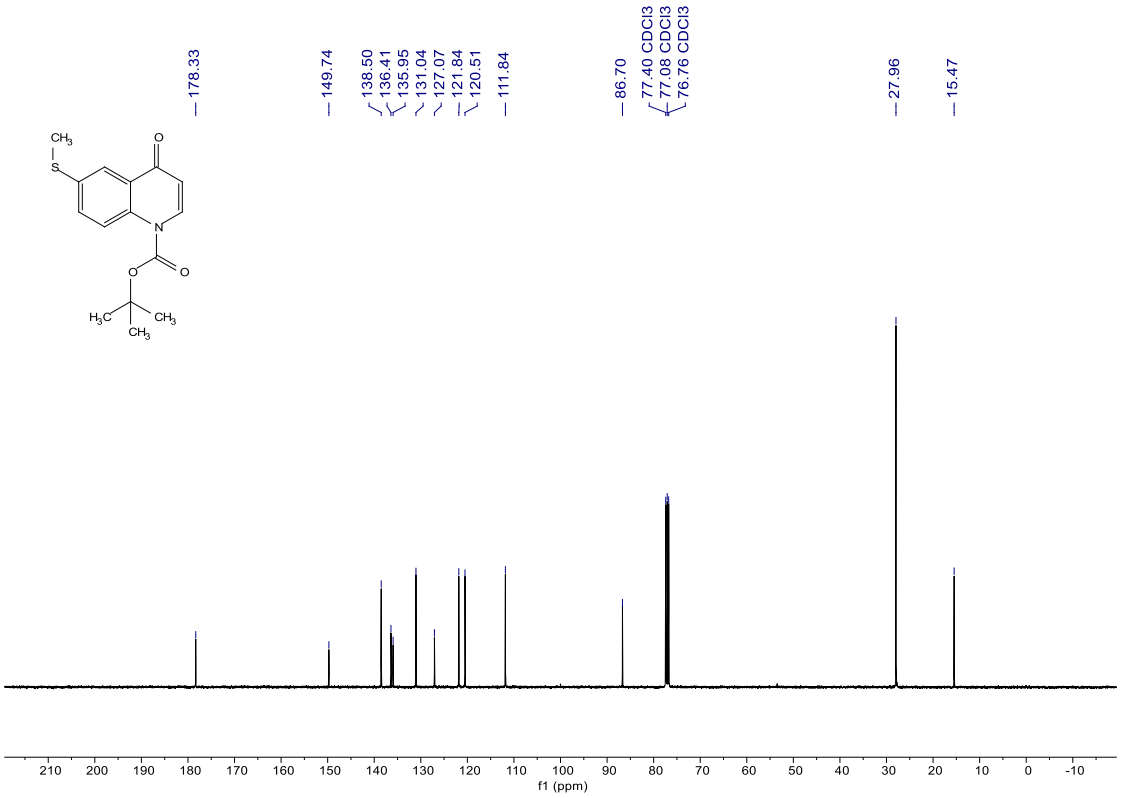


Compound 1m

^{1}H NMR (400 MHz, $CDCl_3$)

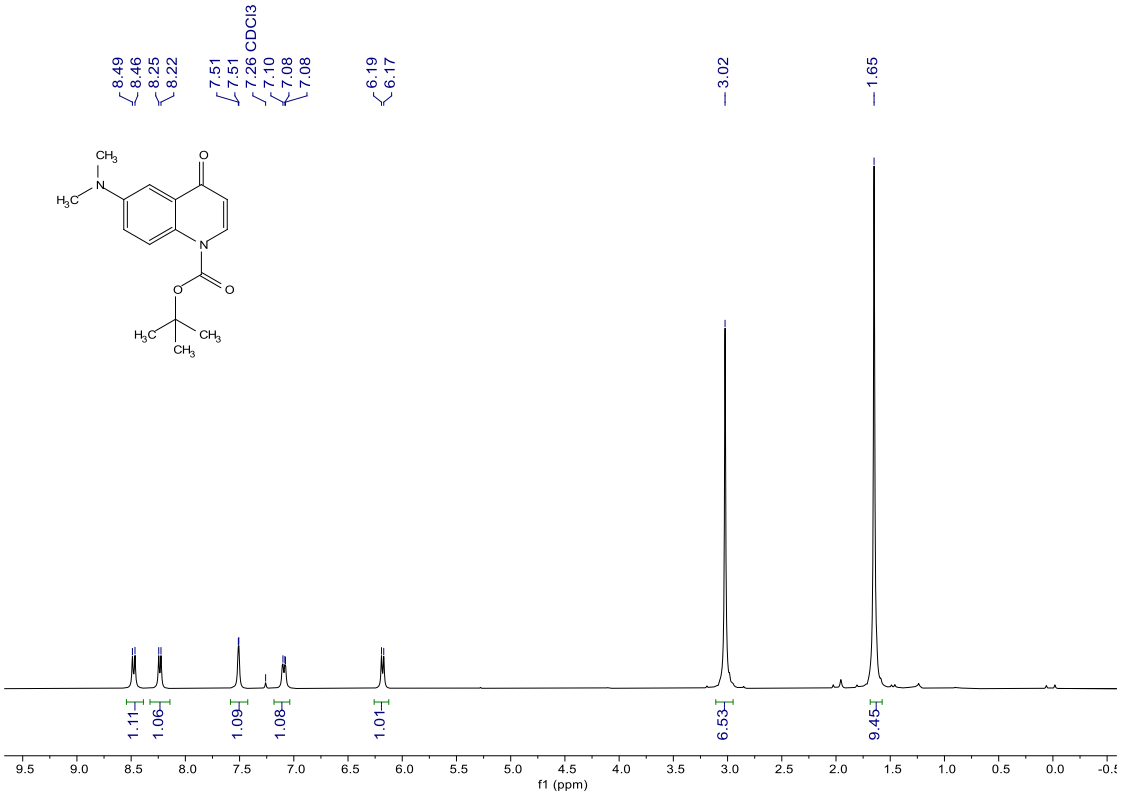


^{13}C NMR (101 MHz, $CDCl_3$)

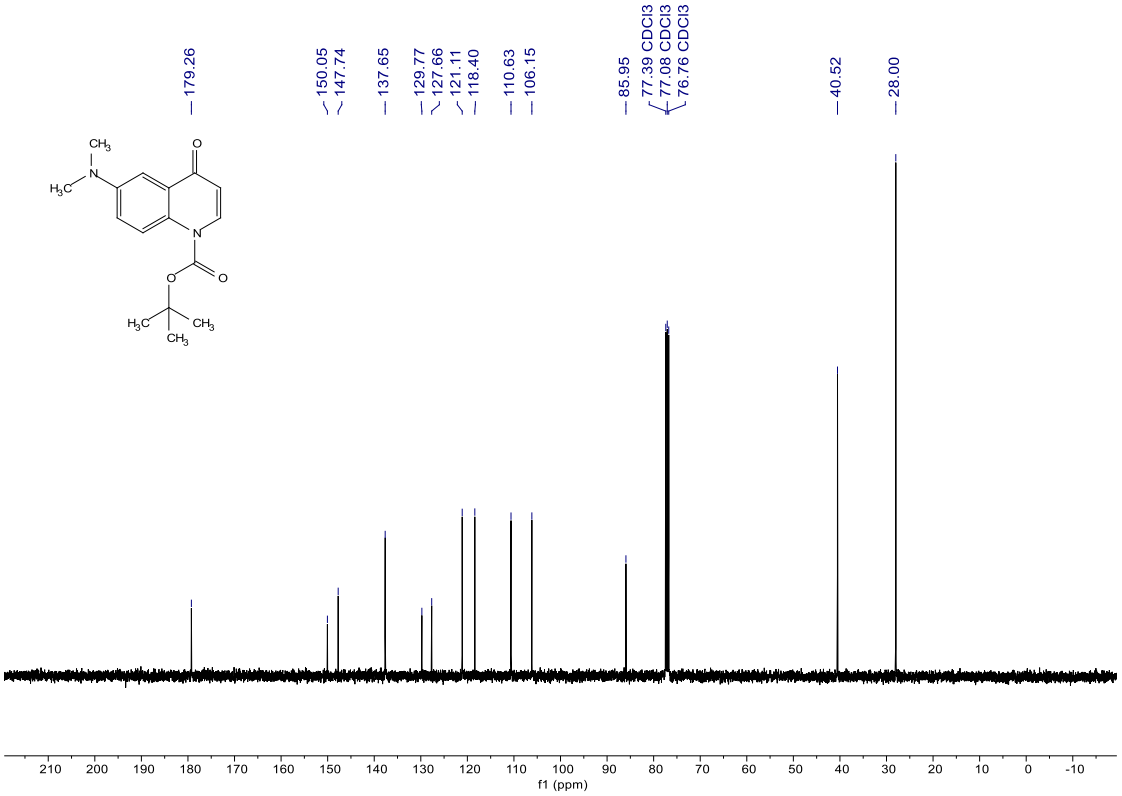


Compound 1n

^{1}H NMR (400 MHz, $CDCl_3$)

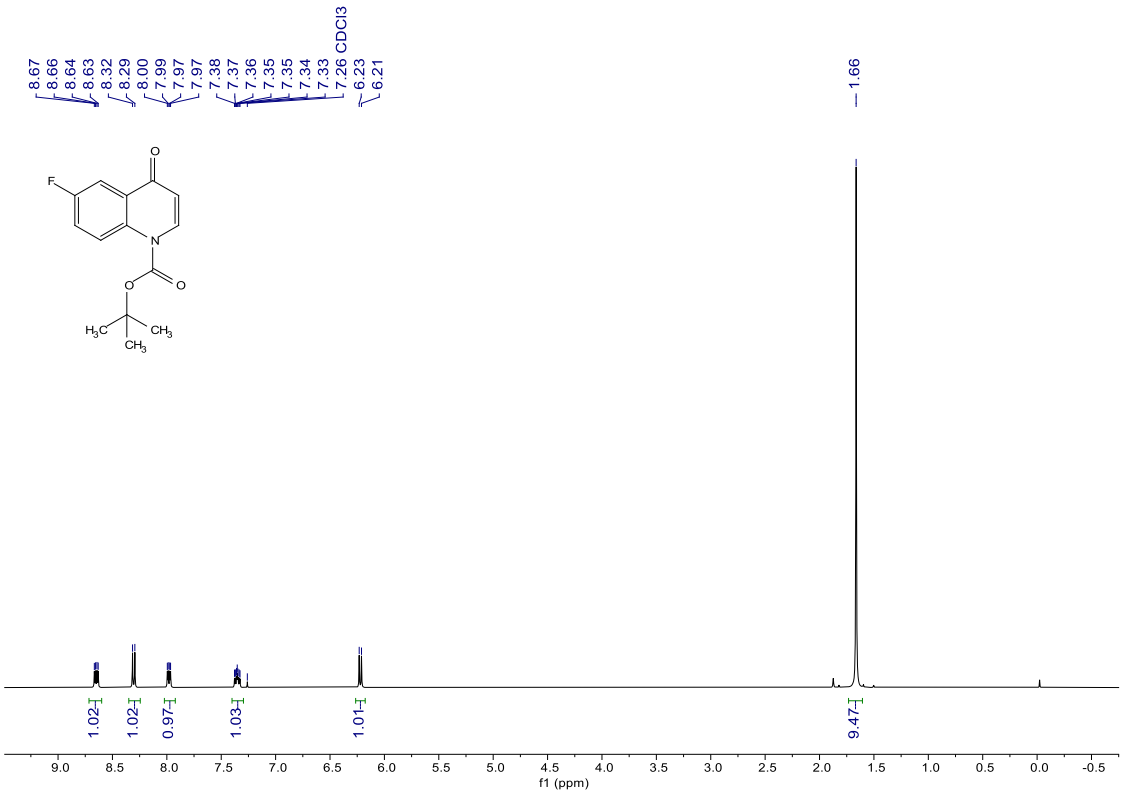


^{13}C NMR (101 MHz, $CDCl_3$)

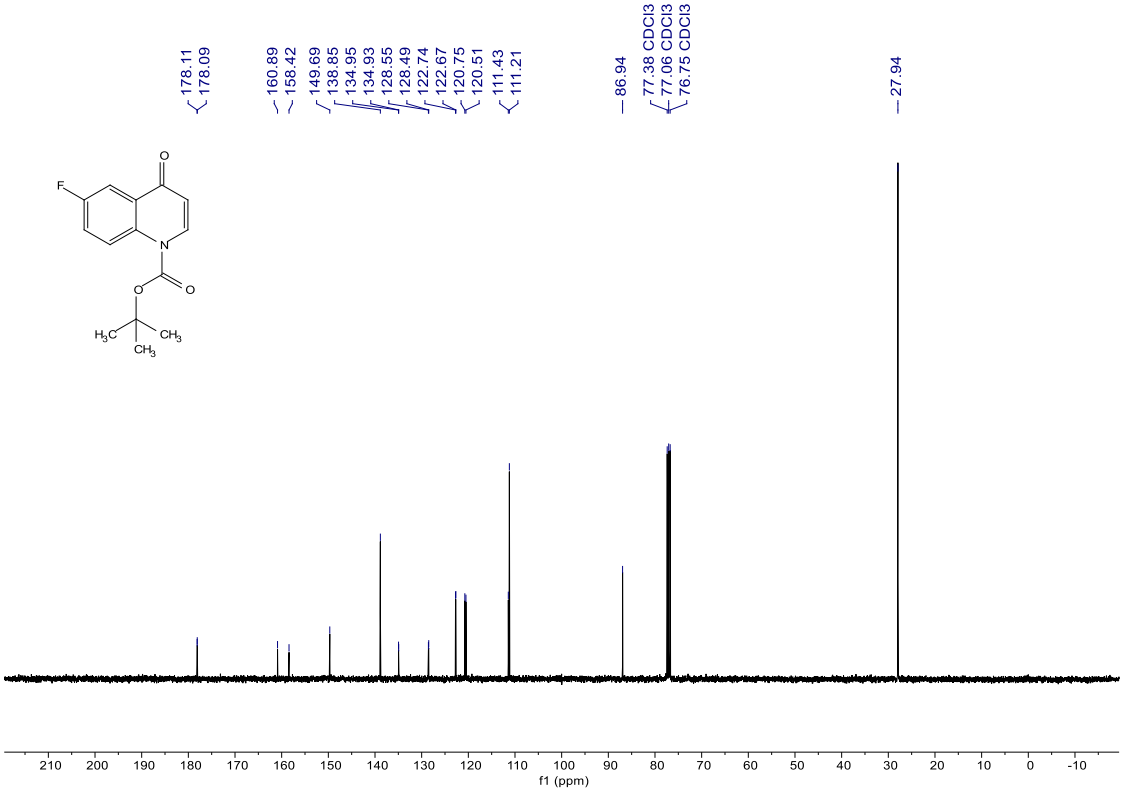


Compound 1o

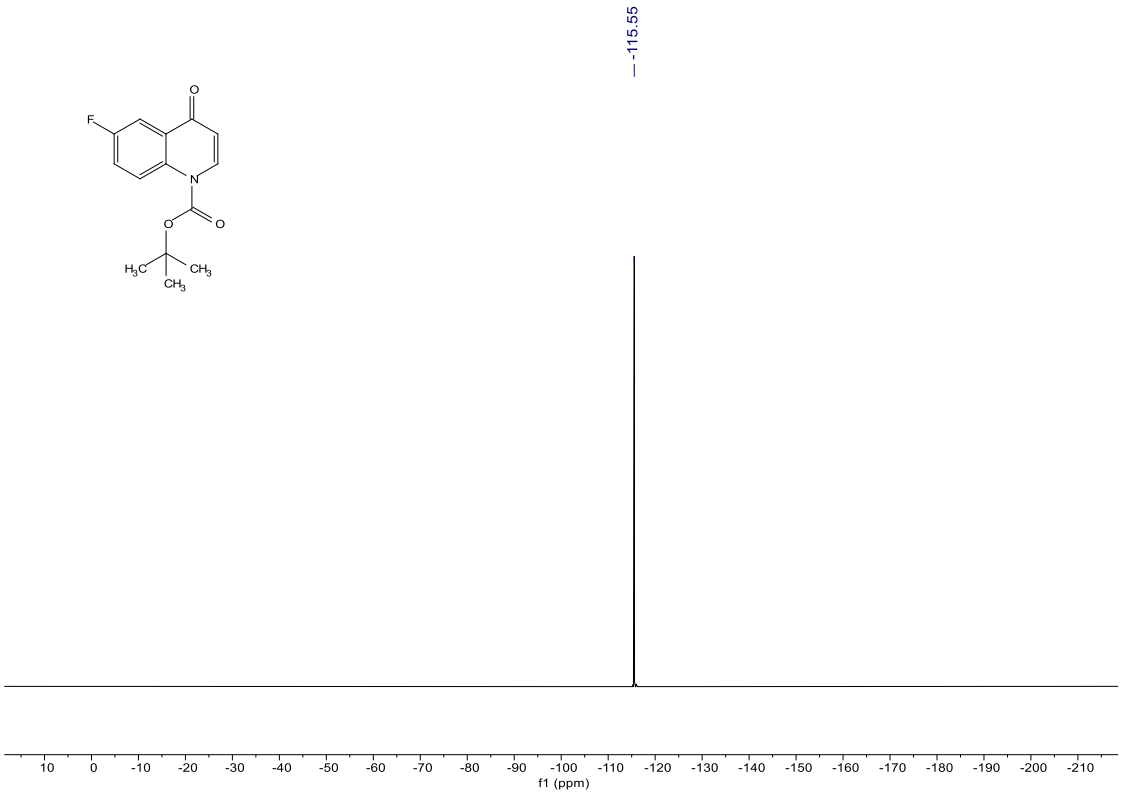
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

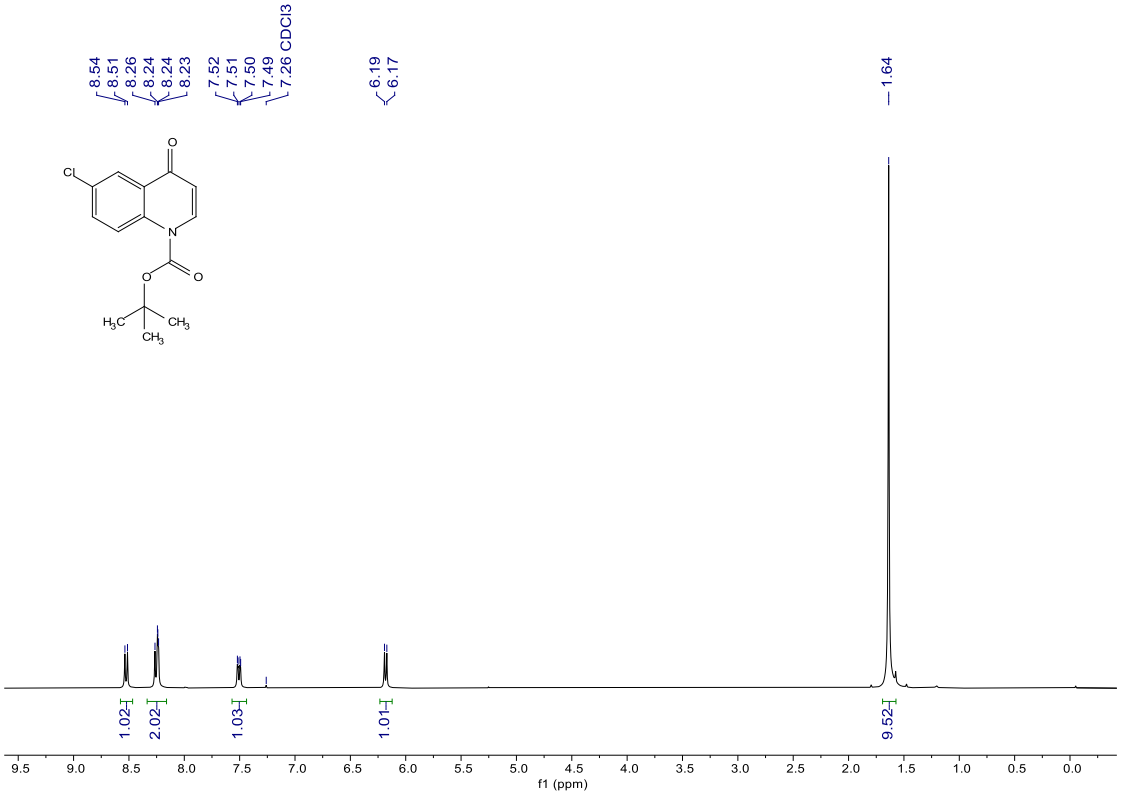


^{19}F NMR (376 MHz, $CDCl_3$)

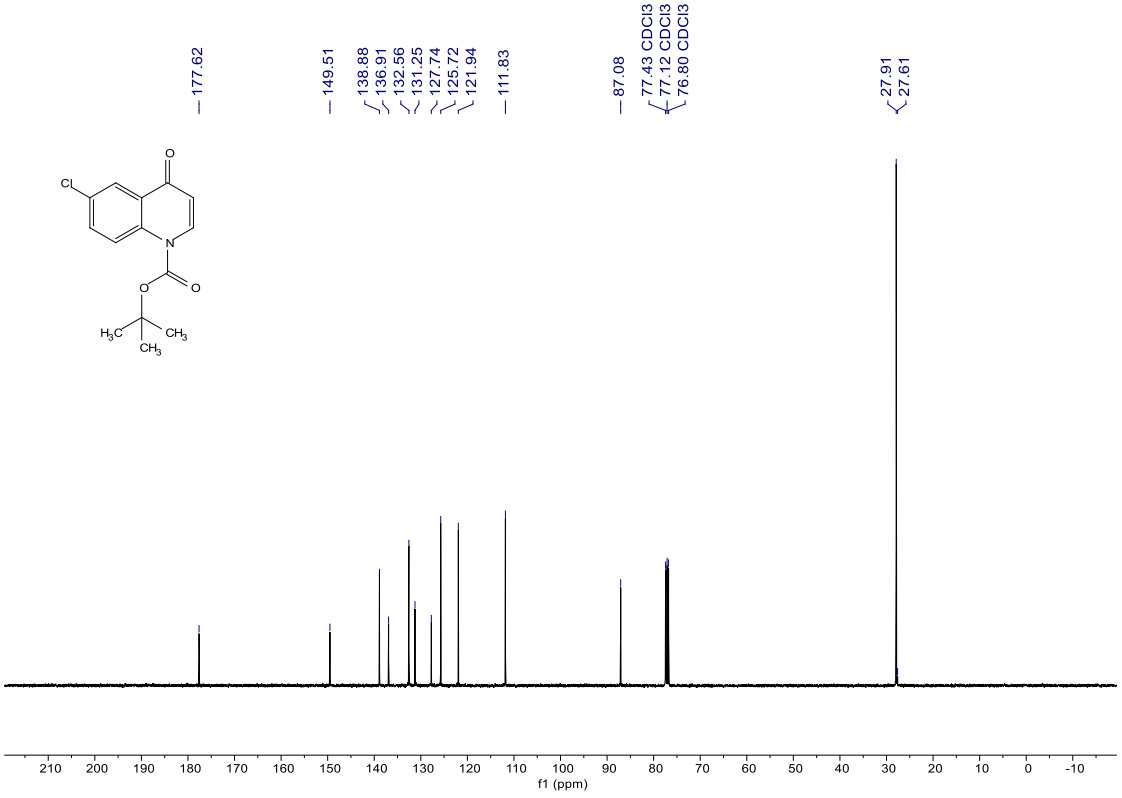


Compound 1p

^{1}H NMR (400 MHz, $CDCl_3$)

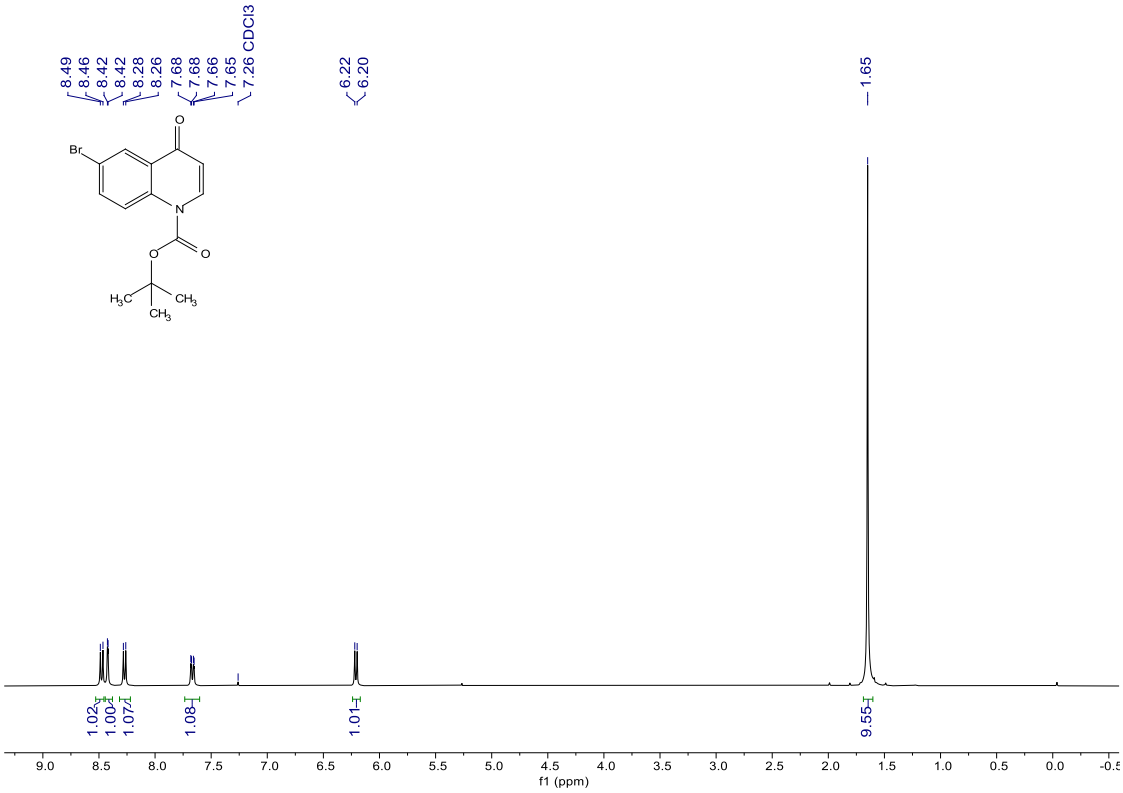


^{13}C NMR (101 MHz, $CDCl_3$)

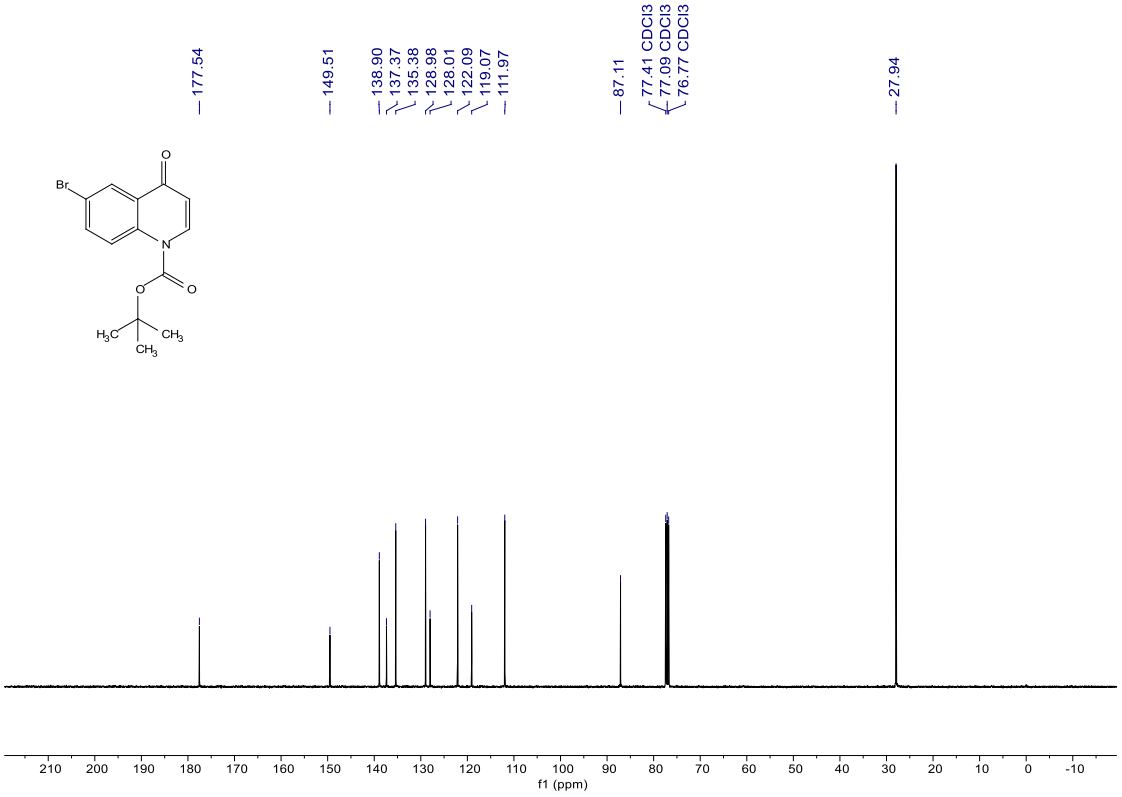


Compound 1q

^{1}H NMR (400 MHz, $CDCl_3$)

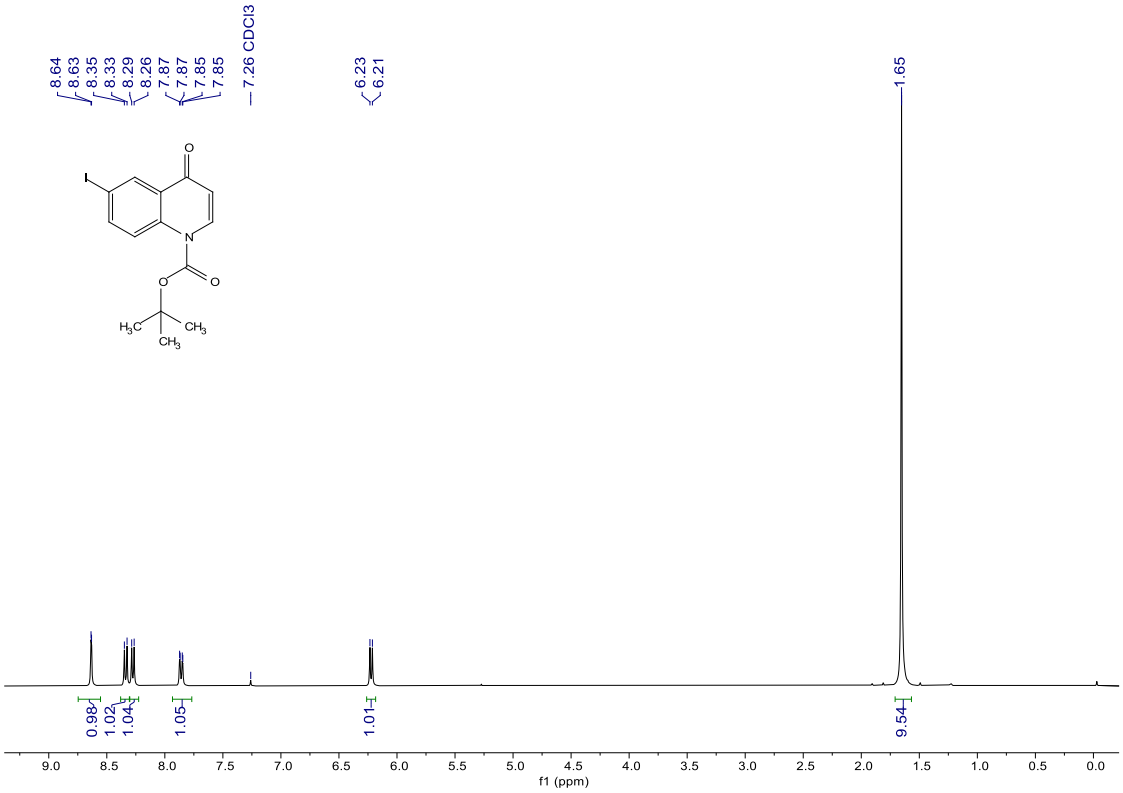


^{13}C NMR (101 MHz, $CDCl_3$)

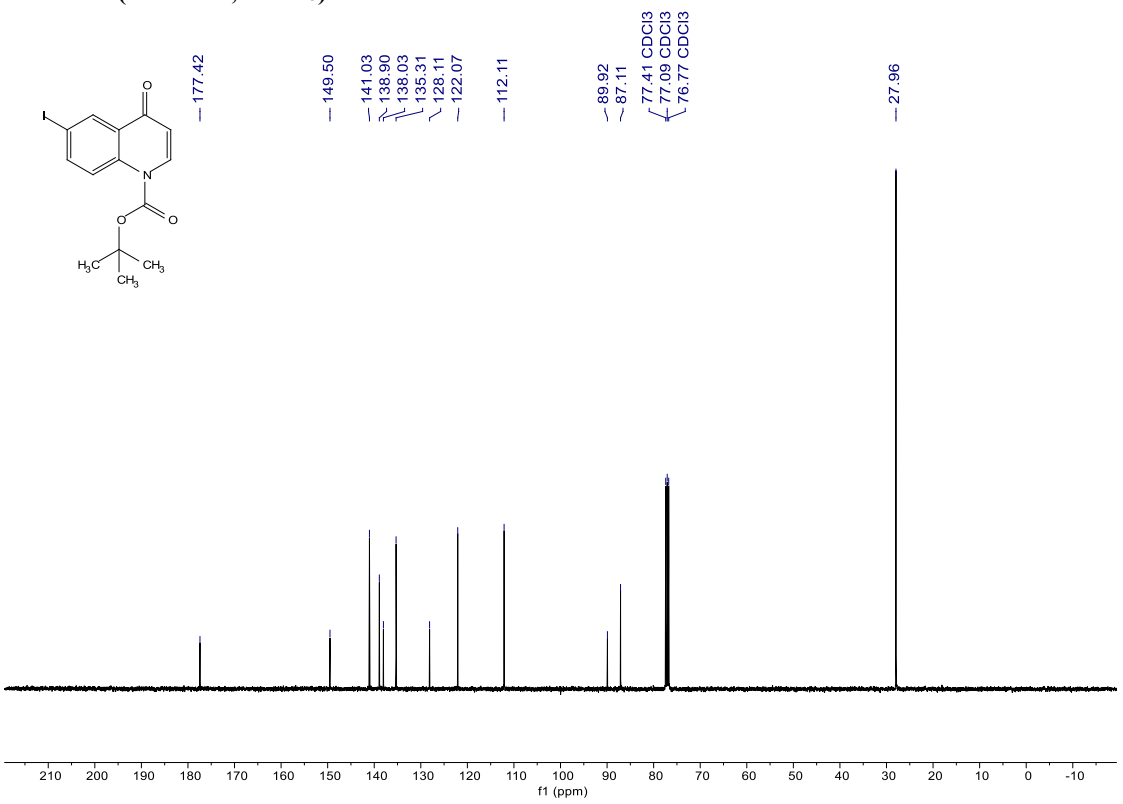


Compound 1r

^{1}H NMR (400 MHz, $CDCl_3$)



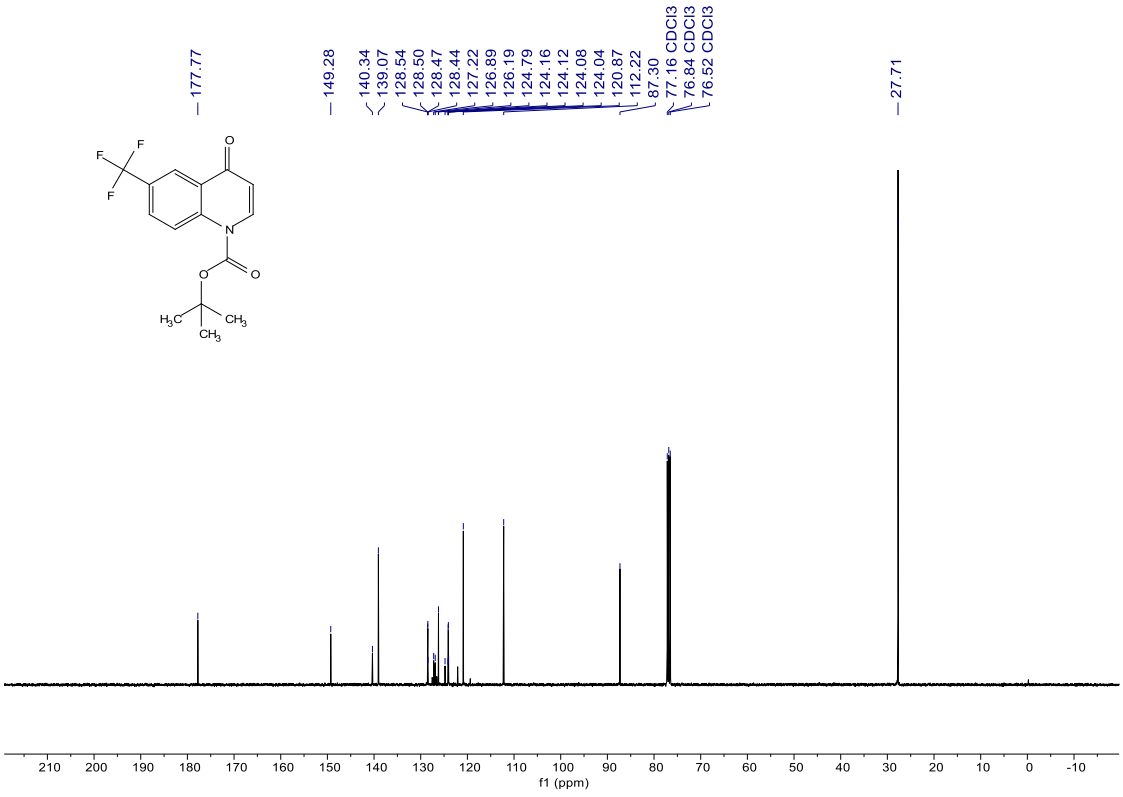
^{13}C NMR (101 MHz, $CDCl_3$)



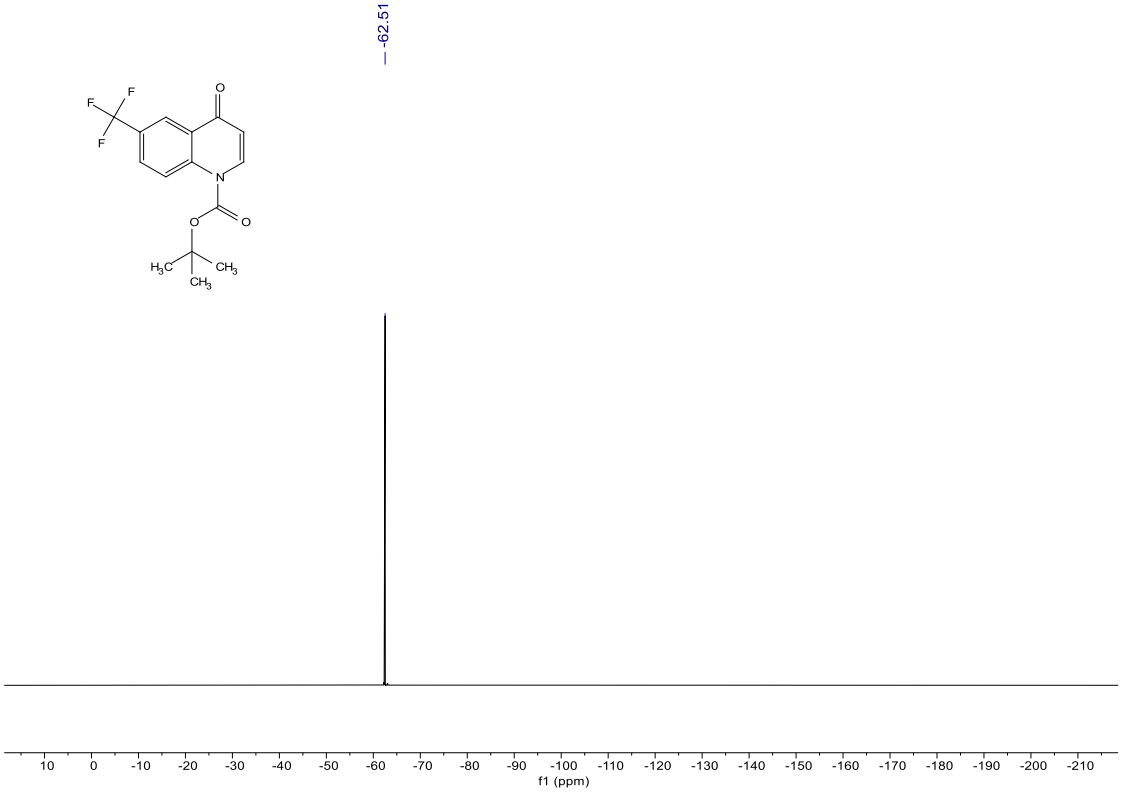
Compound 1s

^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$)

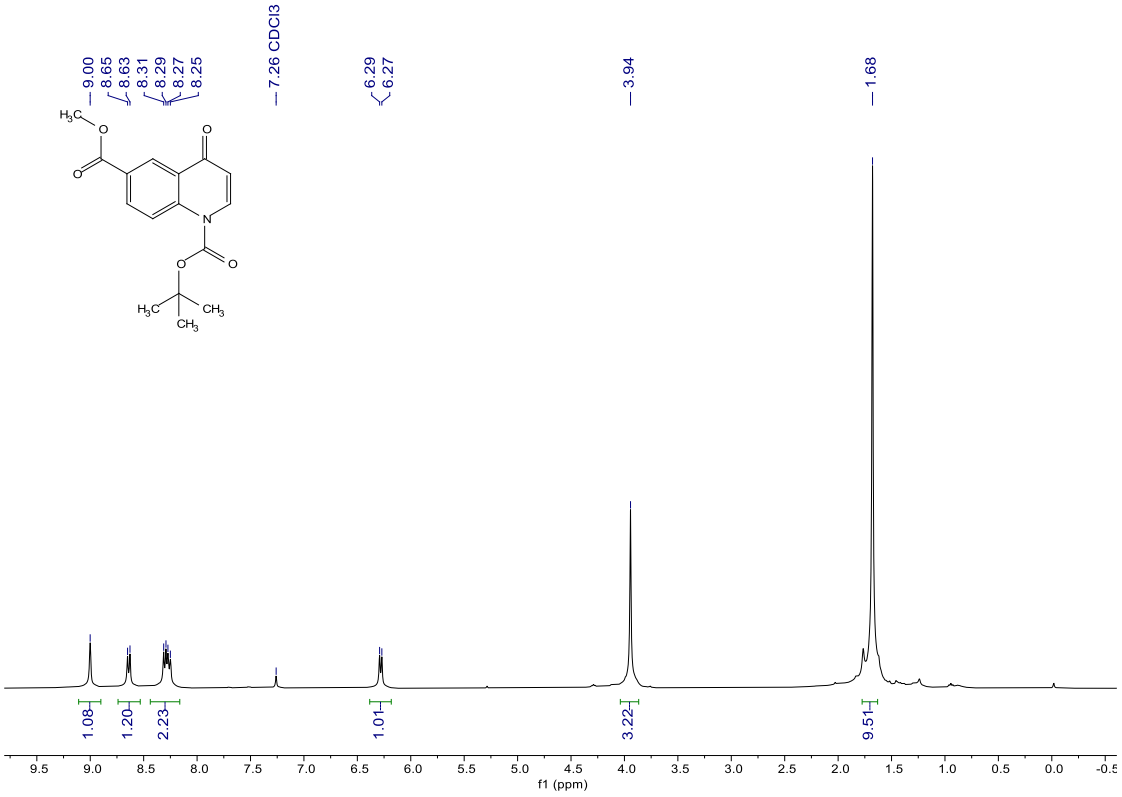


^{19}F NMR (376 MHz, $CDCl_3$)

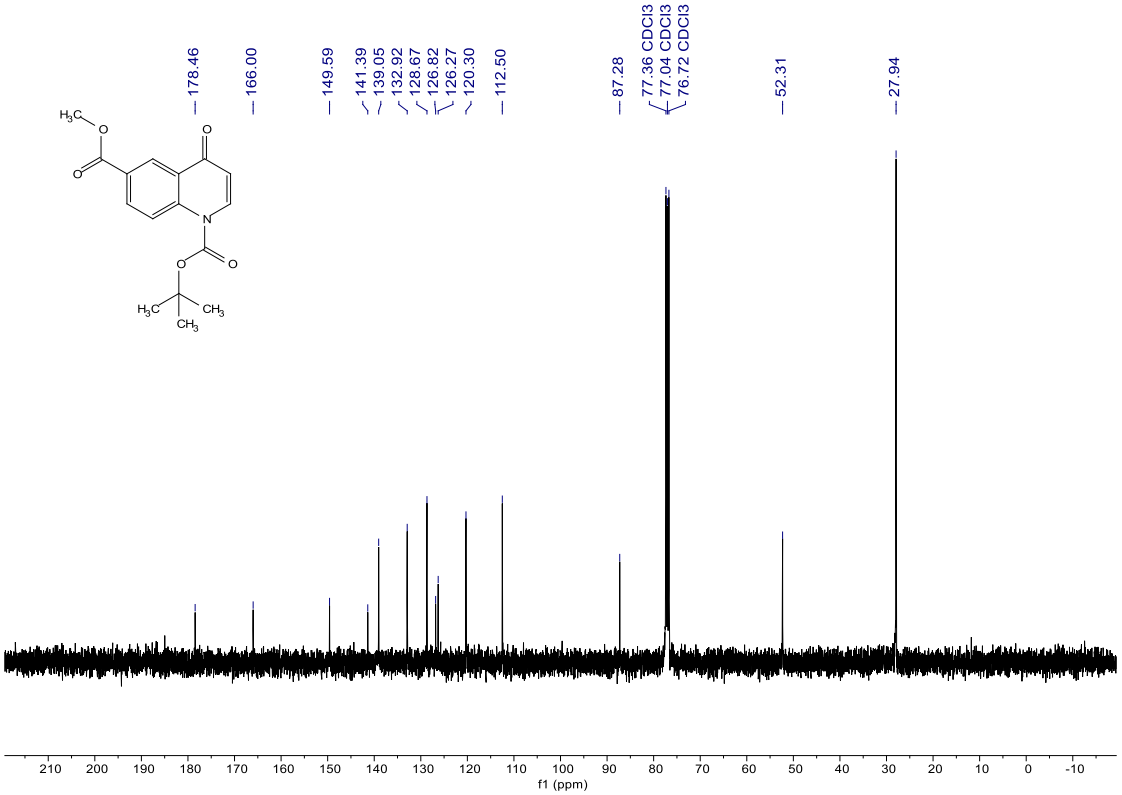


Compound 1t

^{1}H NMR (400 MHz, $CDCl_3$)

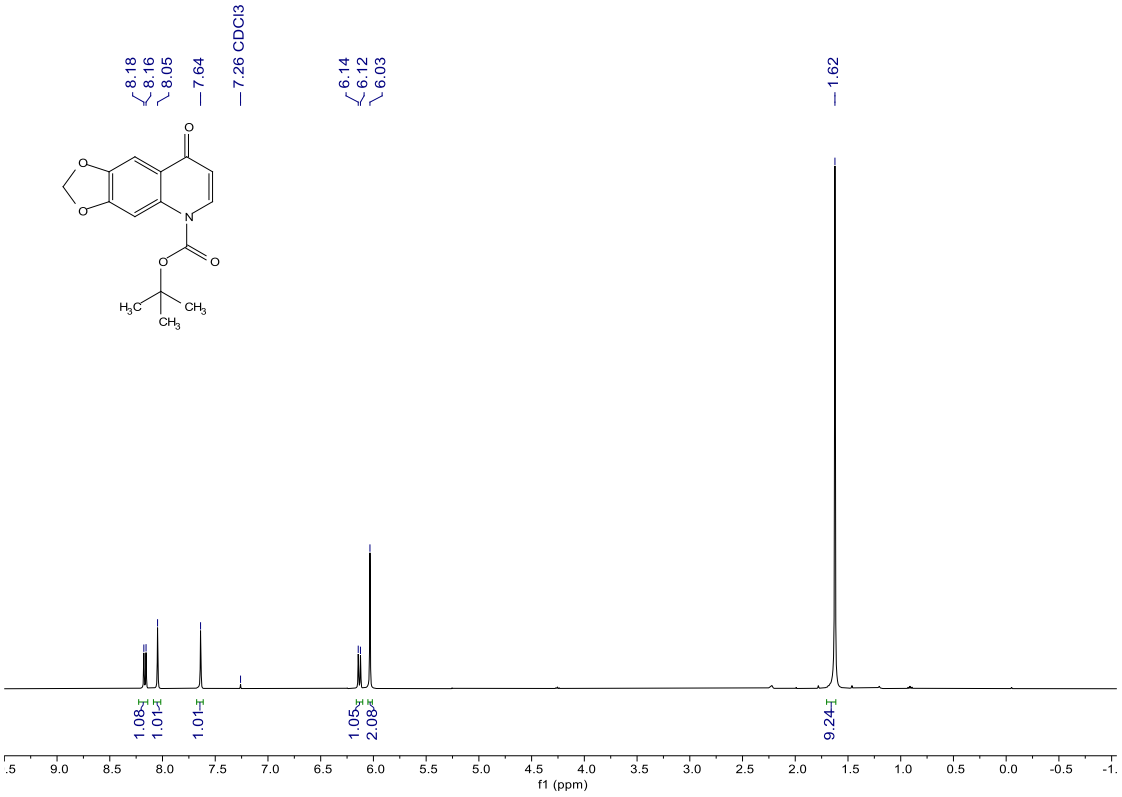


^{13}C NMR (101 MHz, $CDCl_3$)

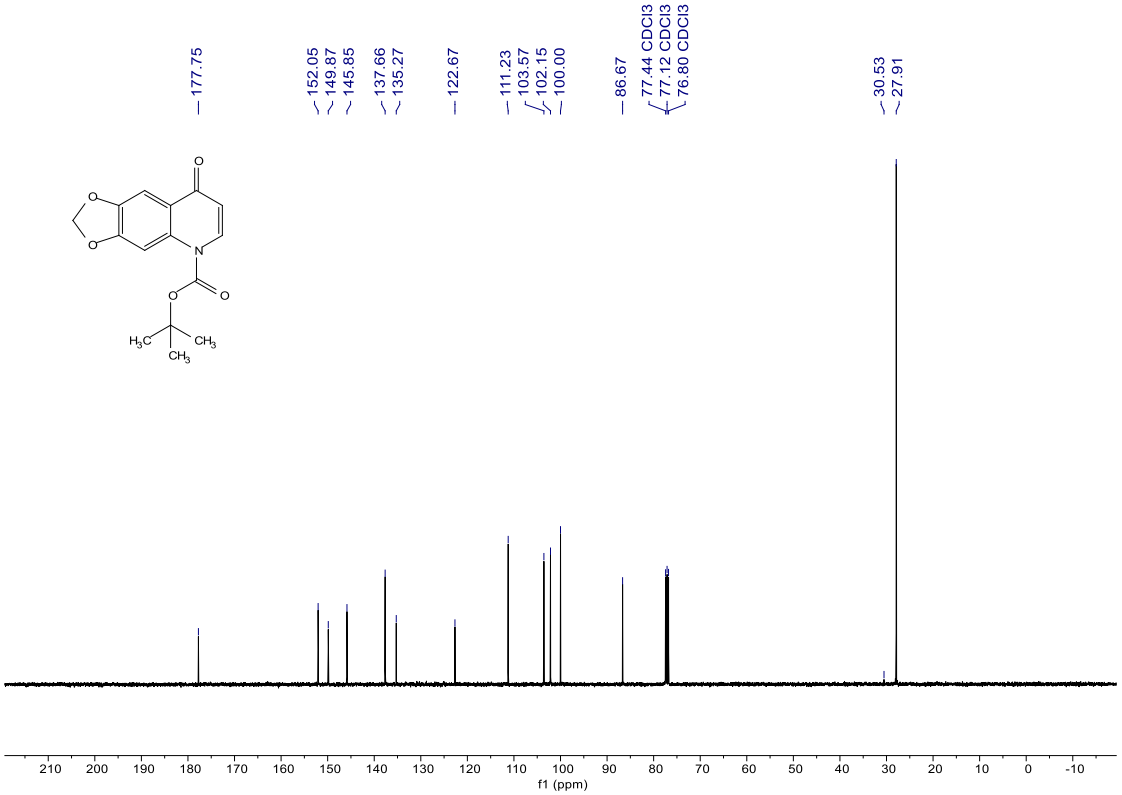


Compound 1u

^{1}H NMR (400 MHz, $CDCl_3$)

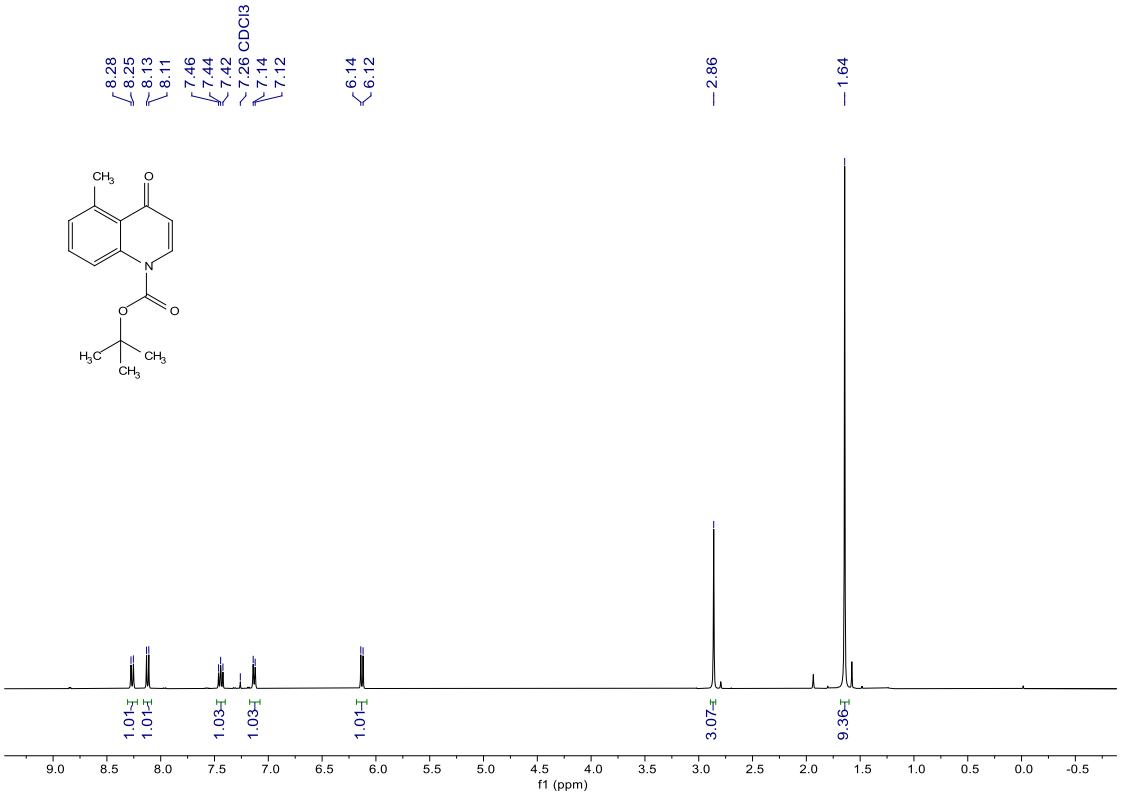


^{13}C NMR (101 MHz, $CDCl_3$)

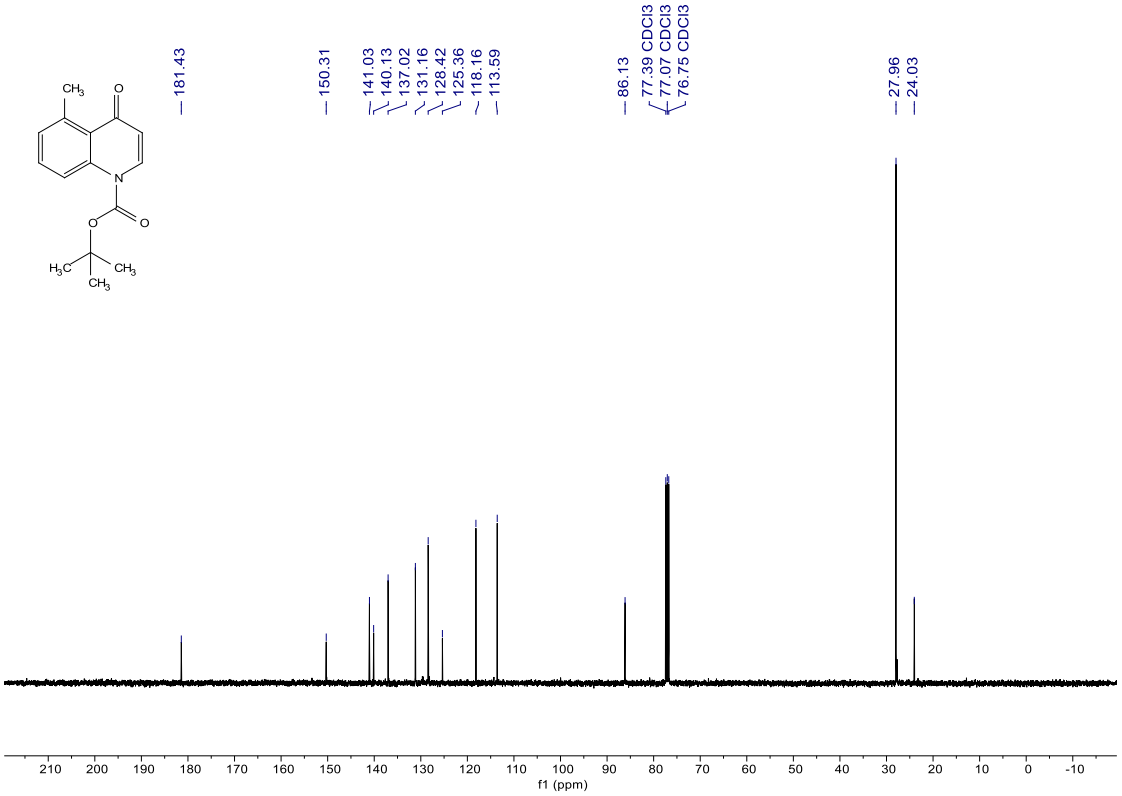


Compound 1v

^{1}H NMR (400 MHz, $CDCl_3$)

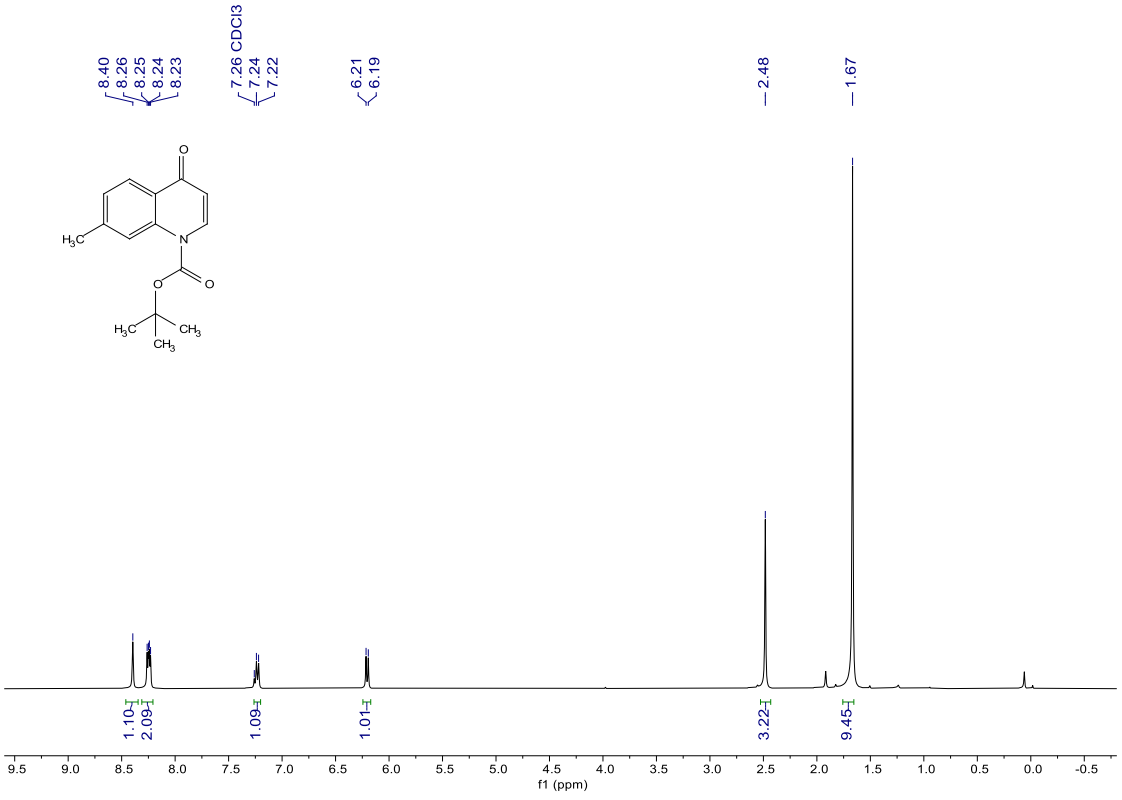


^{13}C NMR (101 MHz, $CDCl_3$)

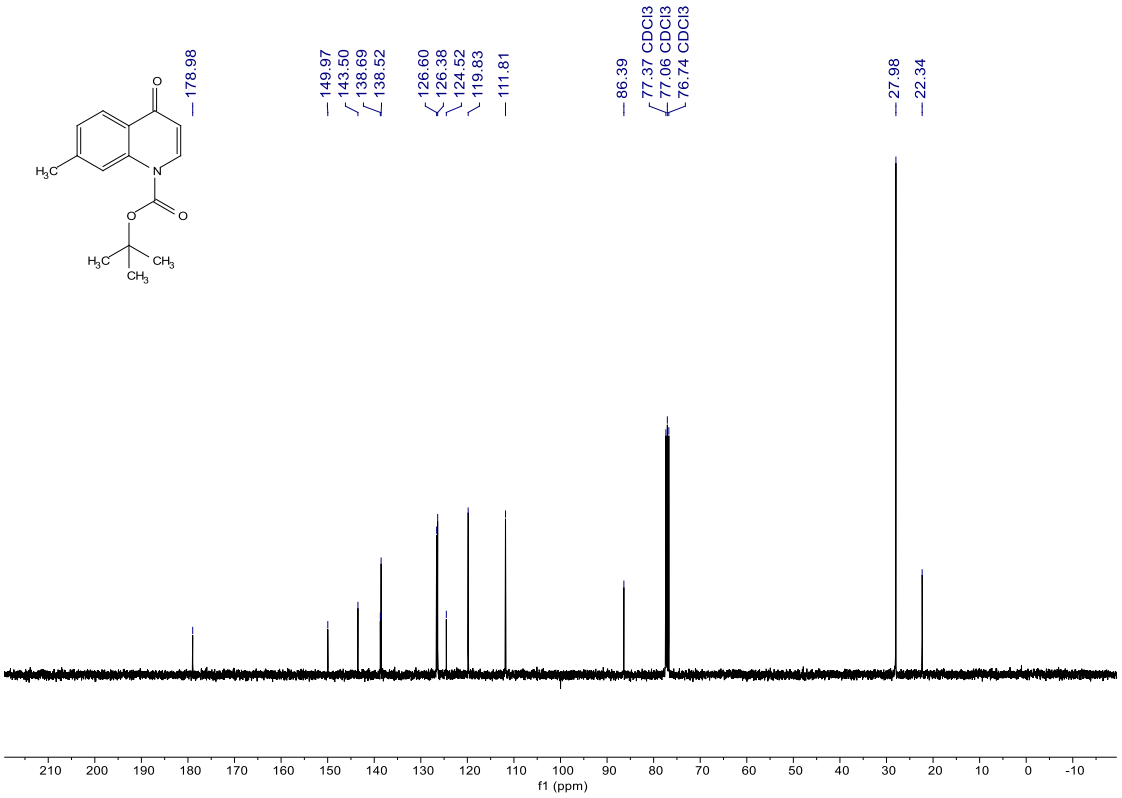


Compound 1w

^{1}H NMR (400 MHz, $CDCl_3$)

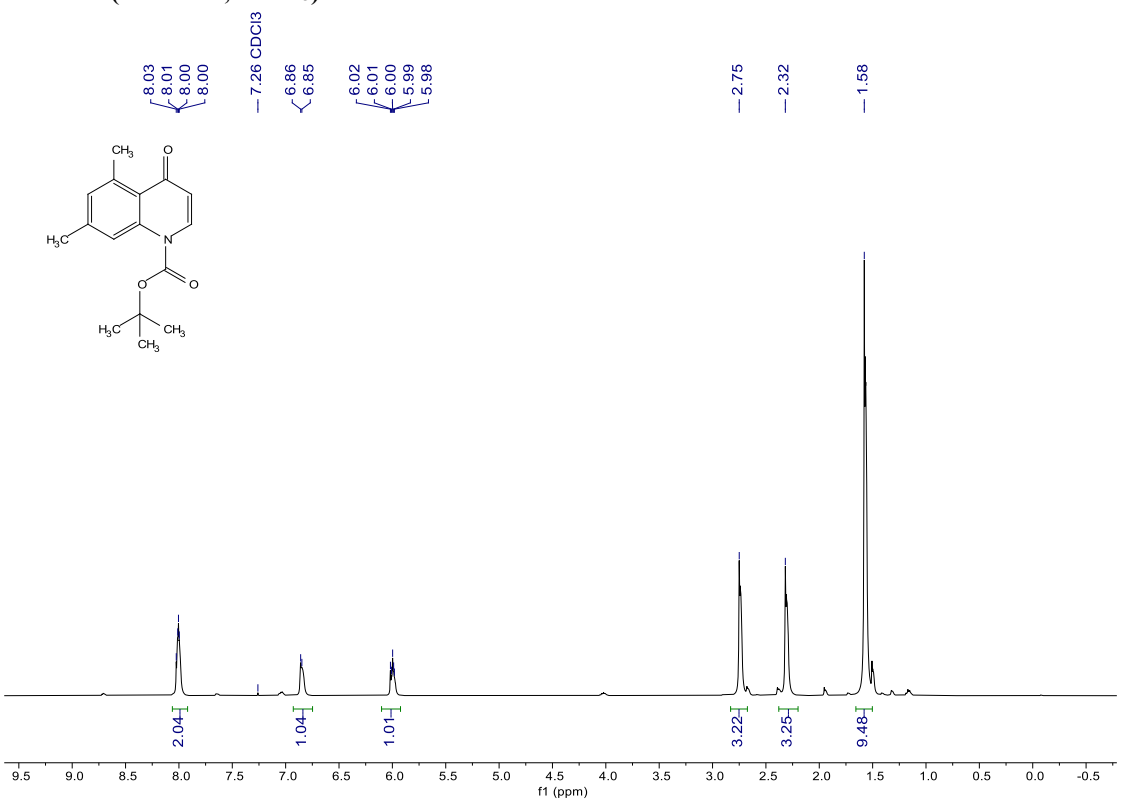


^{13}C NMR (101 MHz, $CDCl_3$)

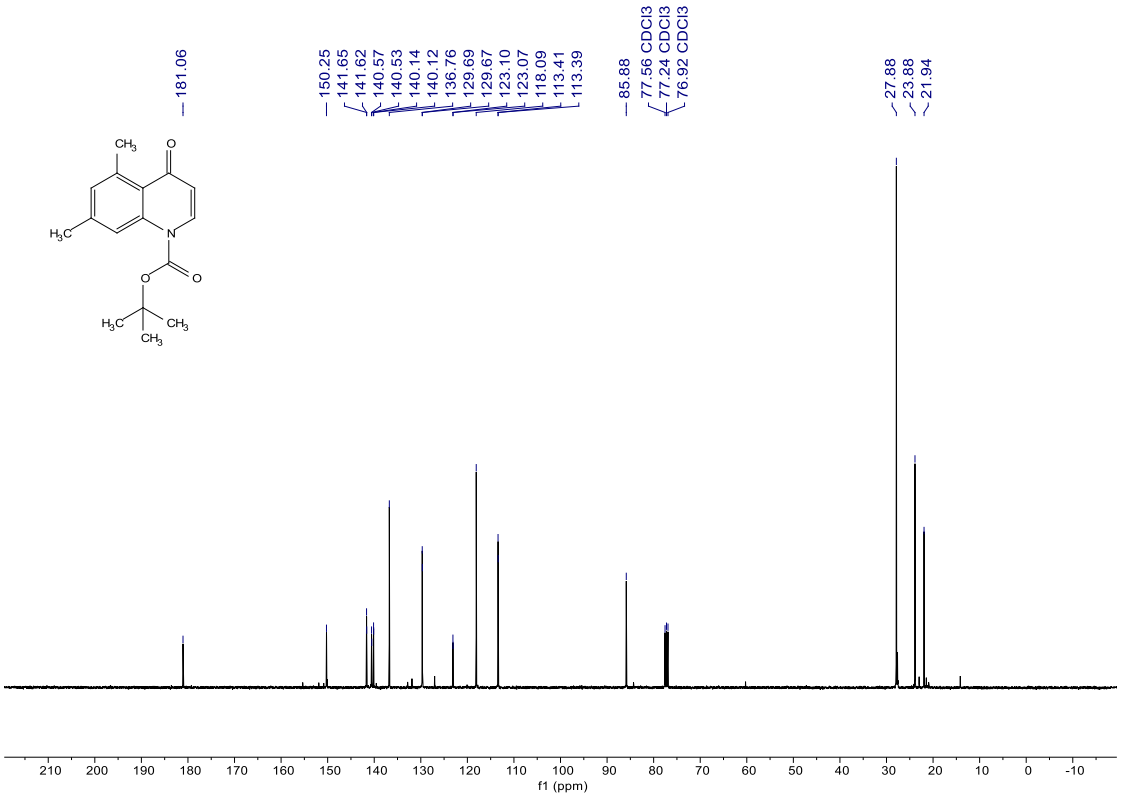


Compound 1x

^{1}H NMR (400 MHz, $CDCl_3$)

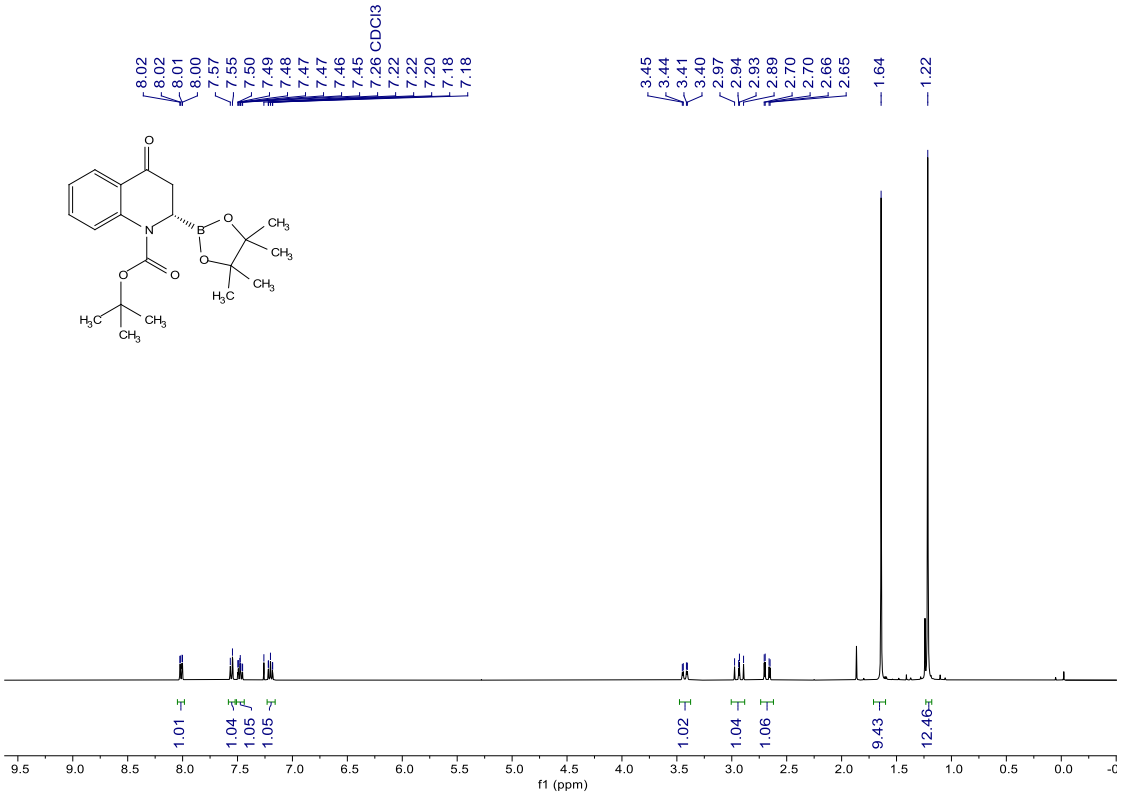


^{13}C NMR (101 MHz, $CDCl_3$)

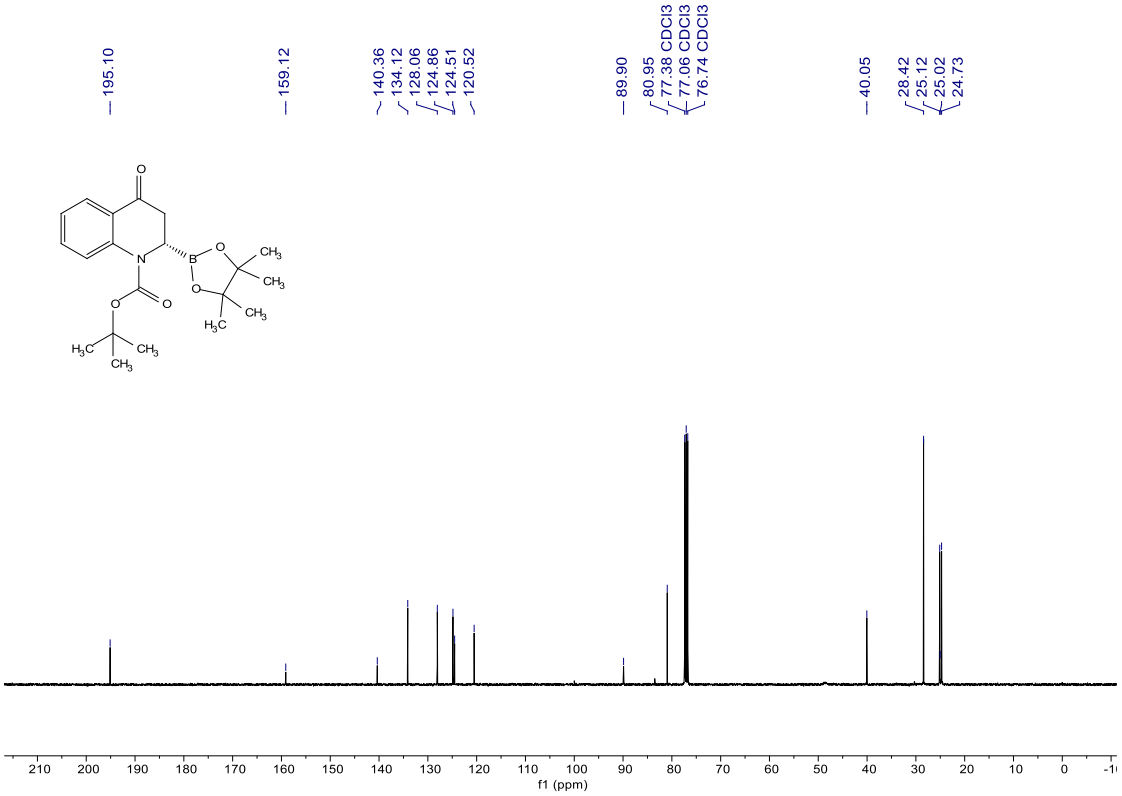


Compound 2a

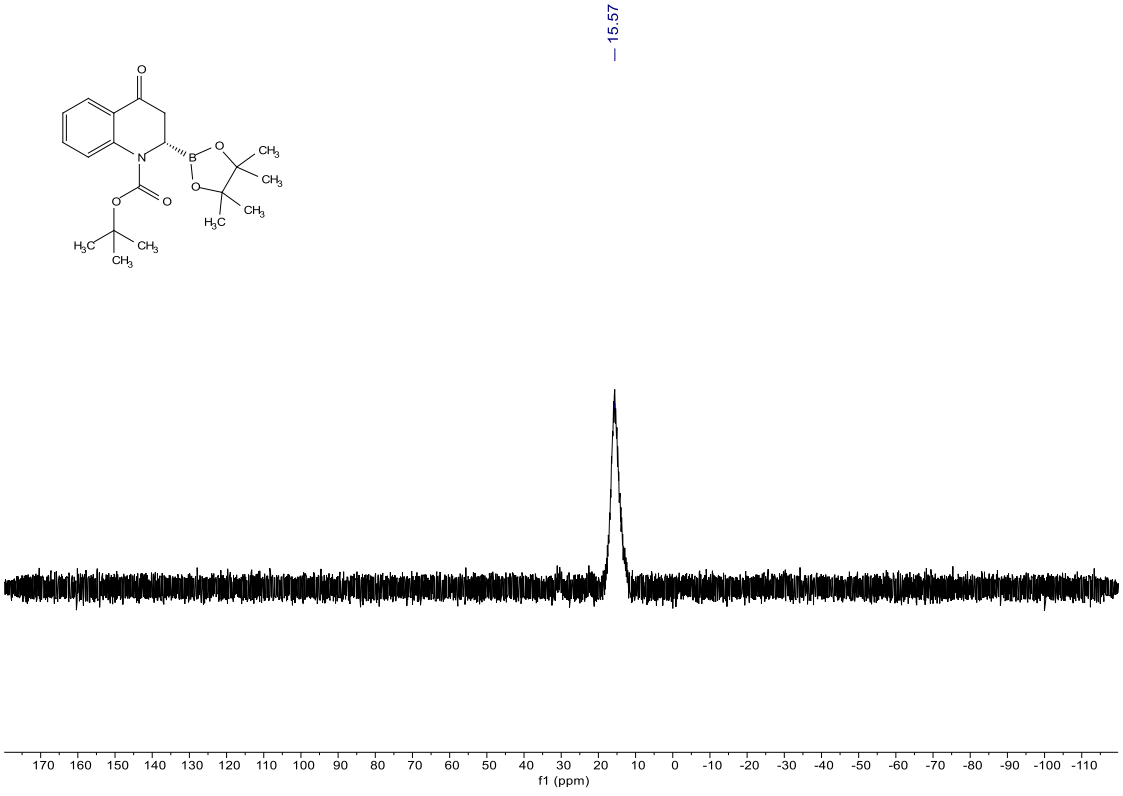
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

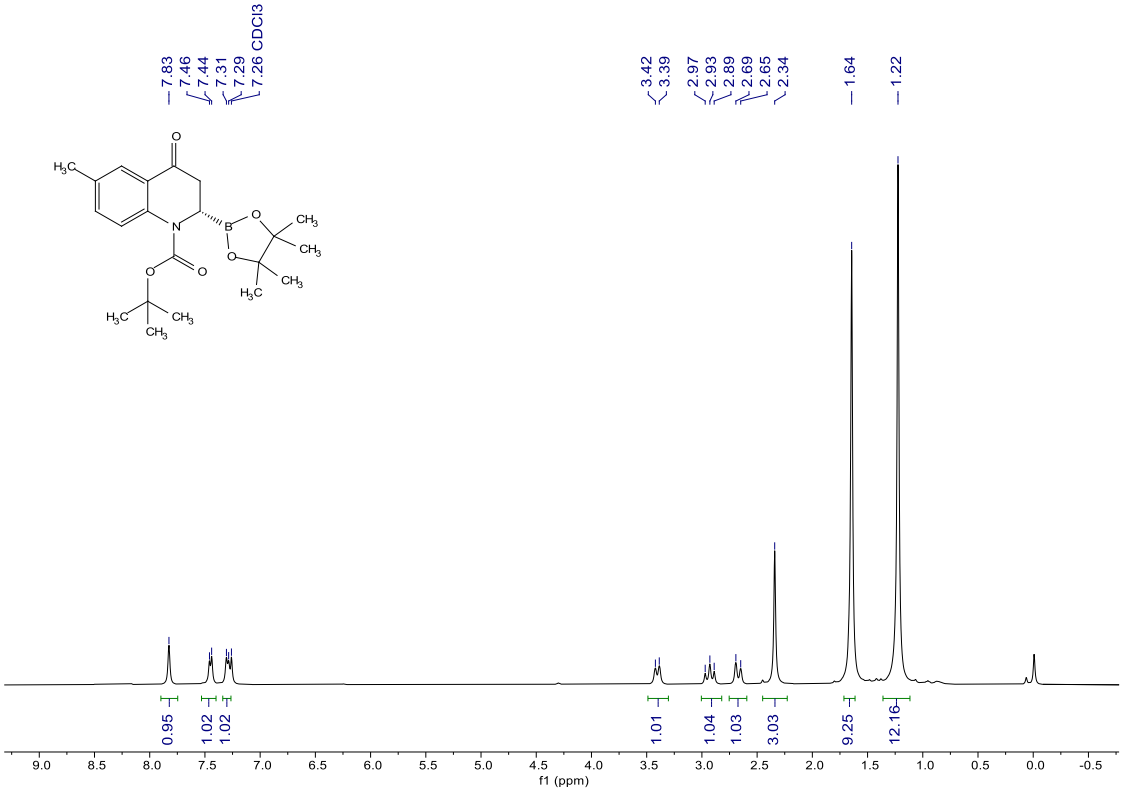


^{11}B NMR (128 MHz, $CDCl_3$)

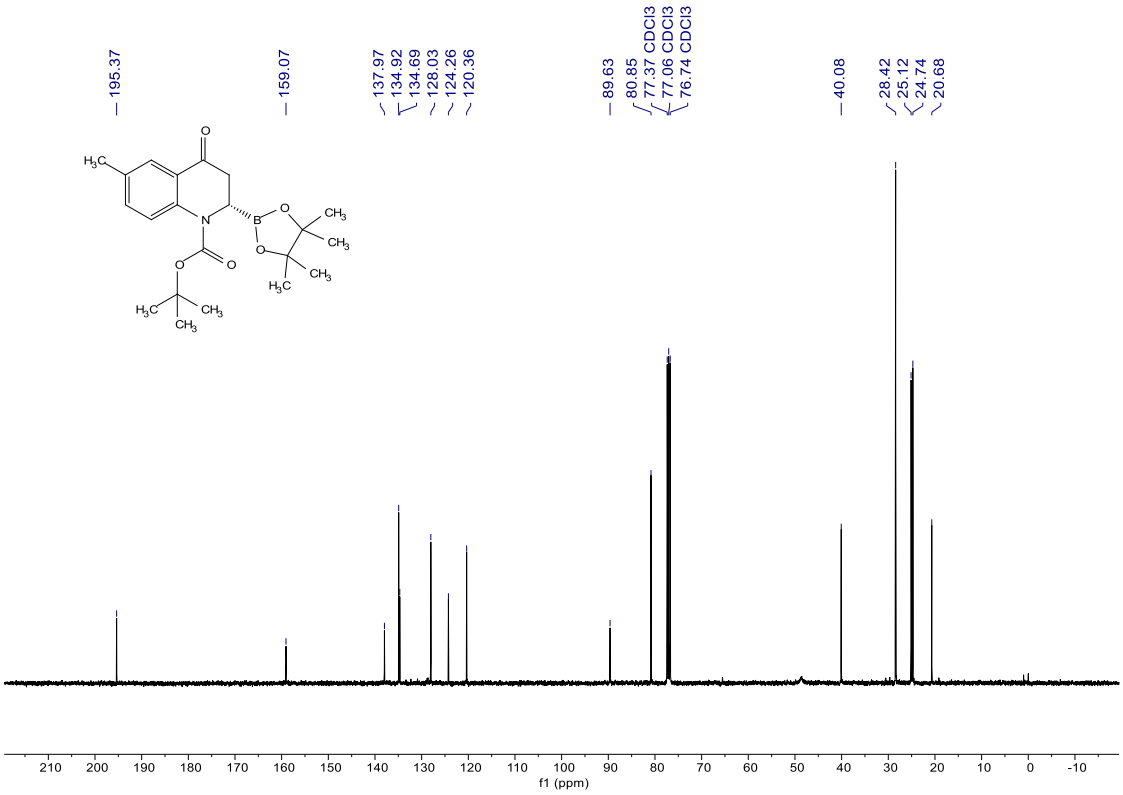


Compound 2b

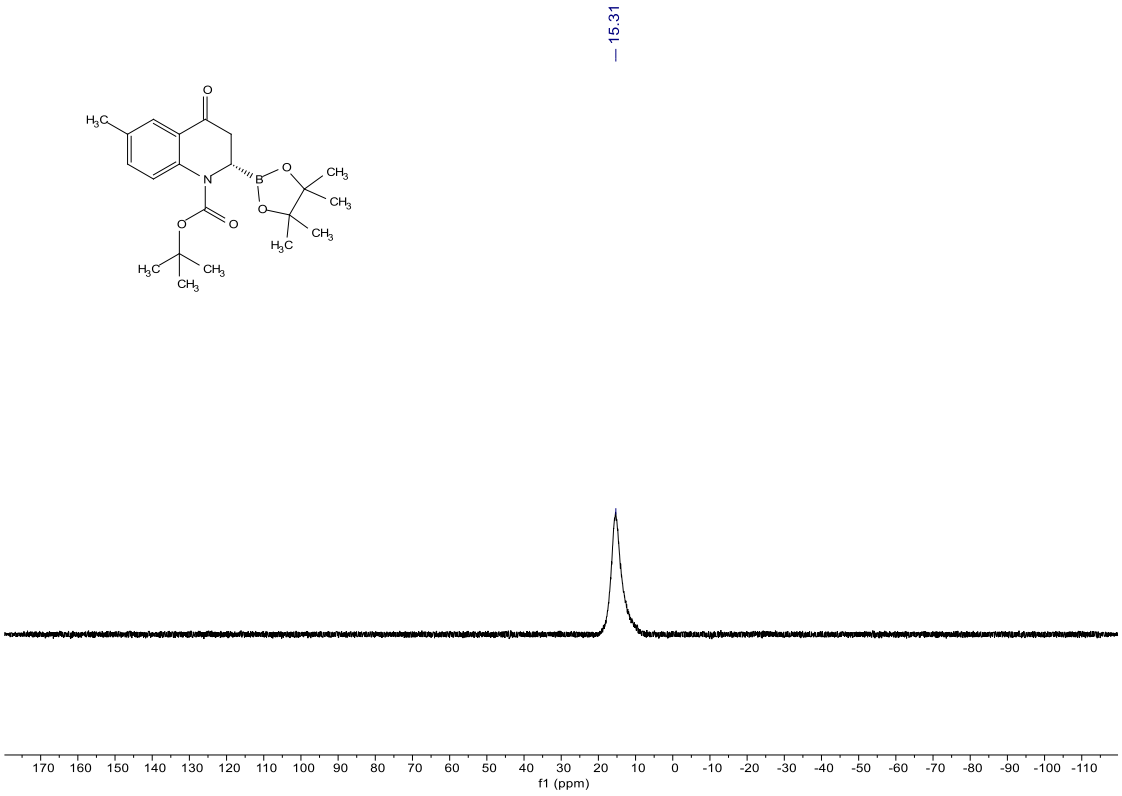
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

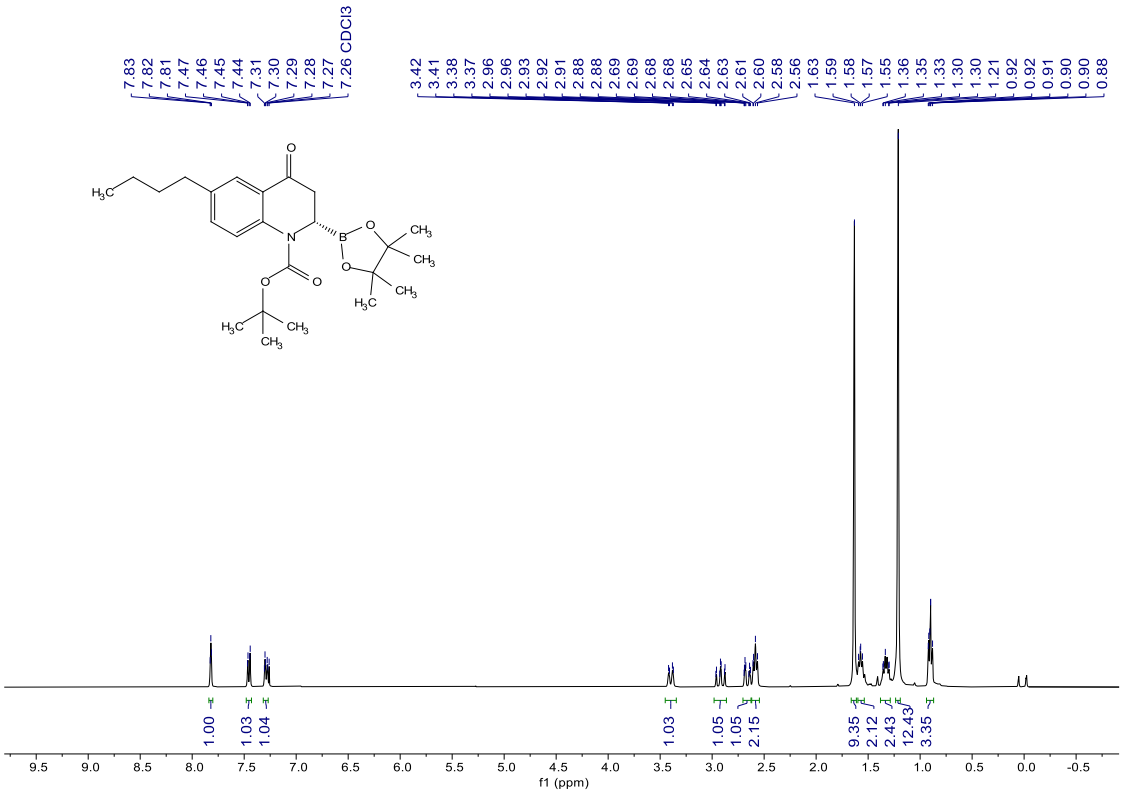


^{11}B NMR (128 MHz, $CDCl_3$)

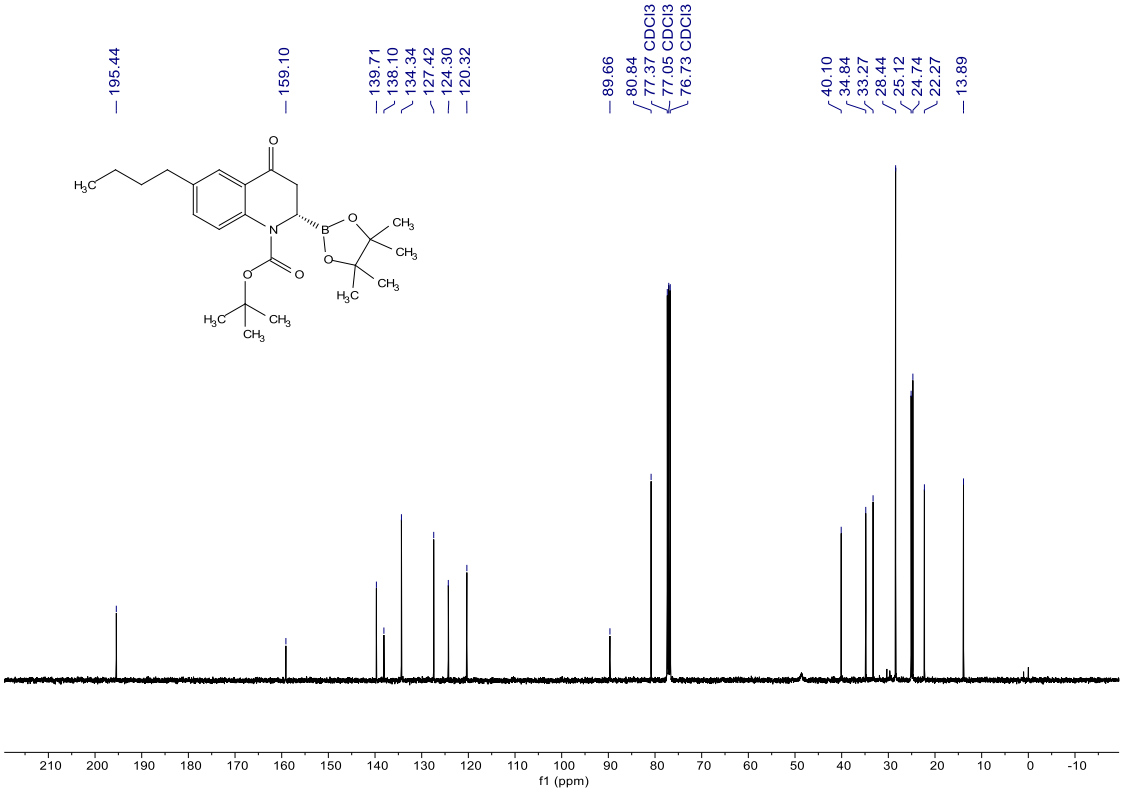


Compound 2c

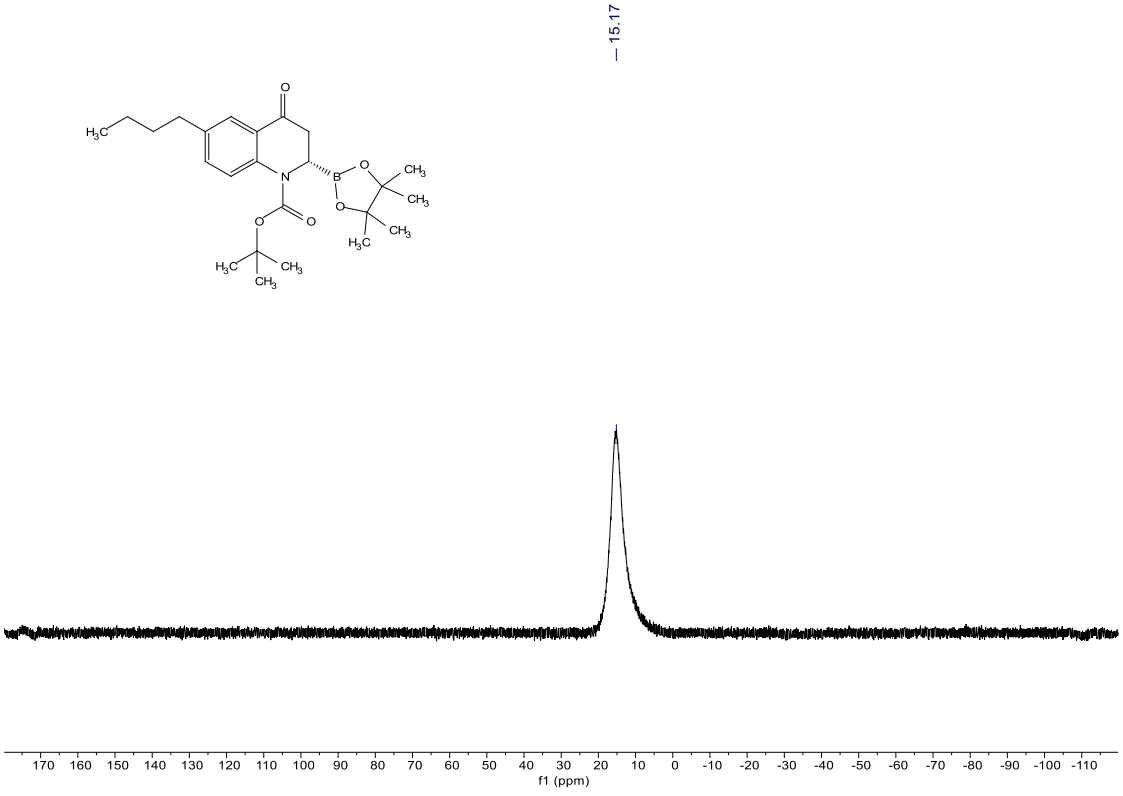
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

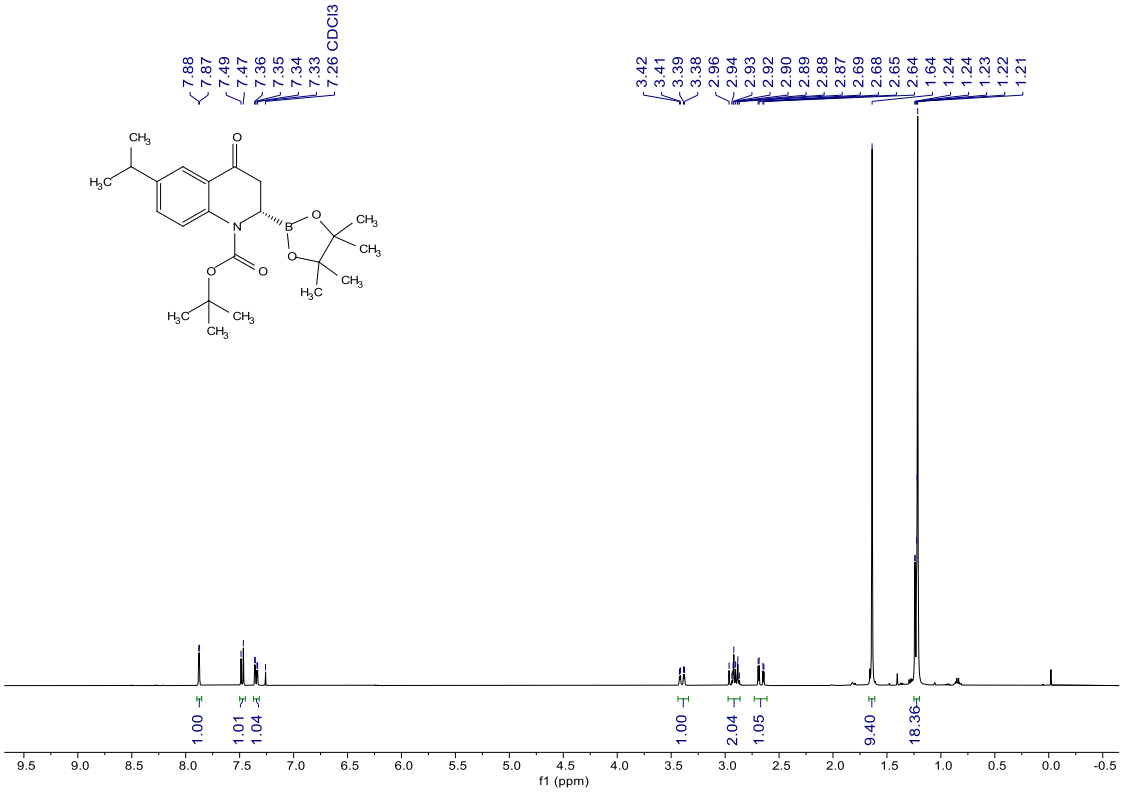


^{11}B NMR (128 MHz, $CDCl_3$)

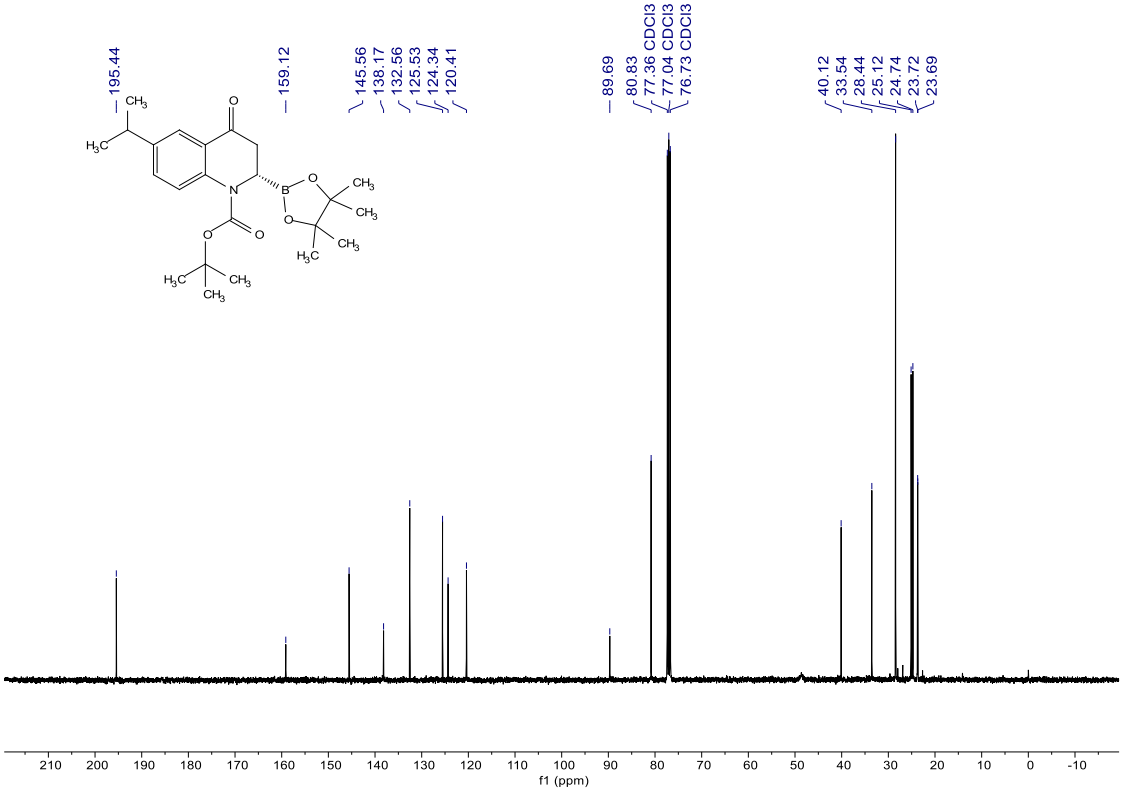


Compound 2d

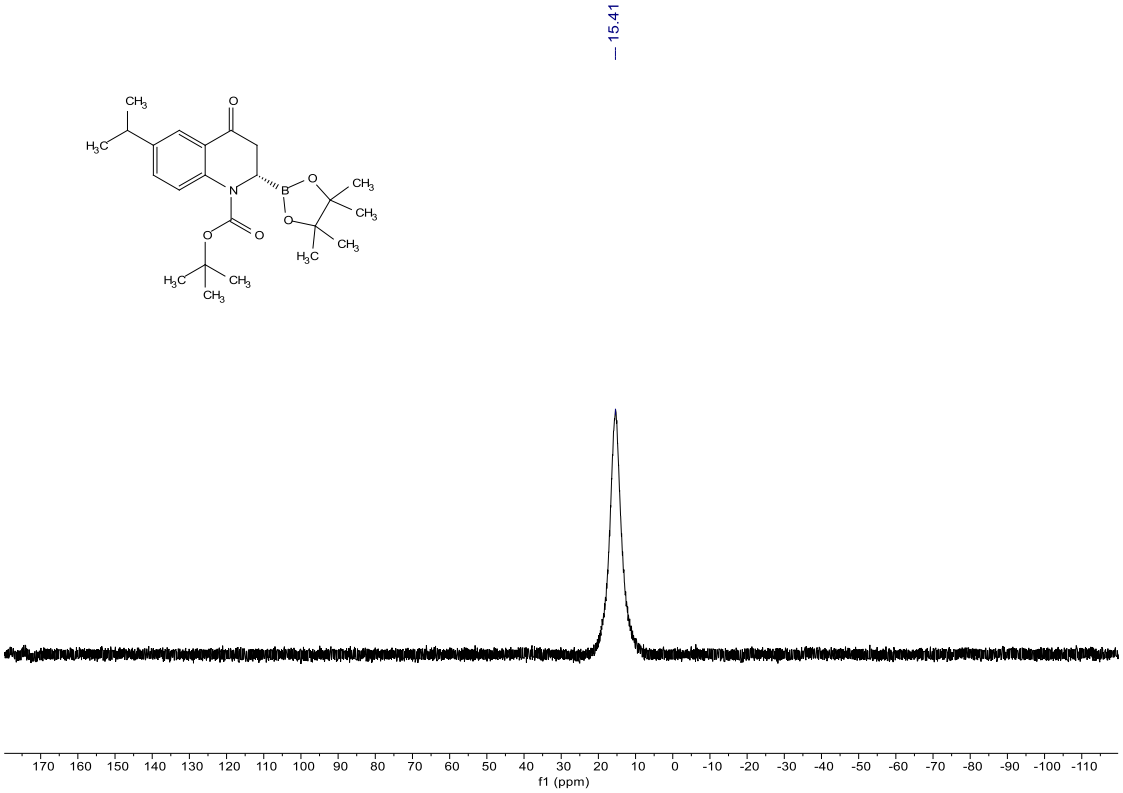
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

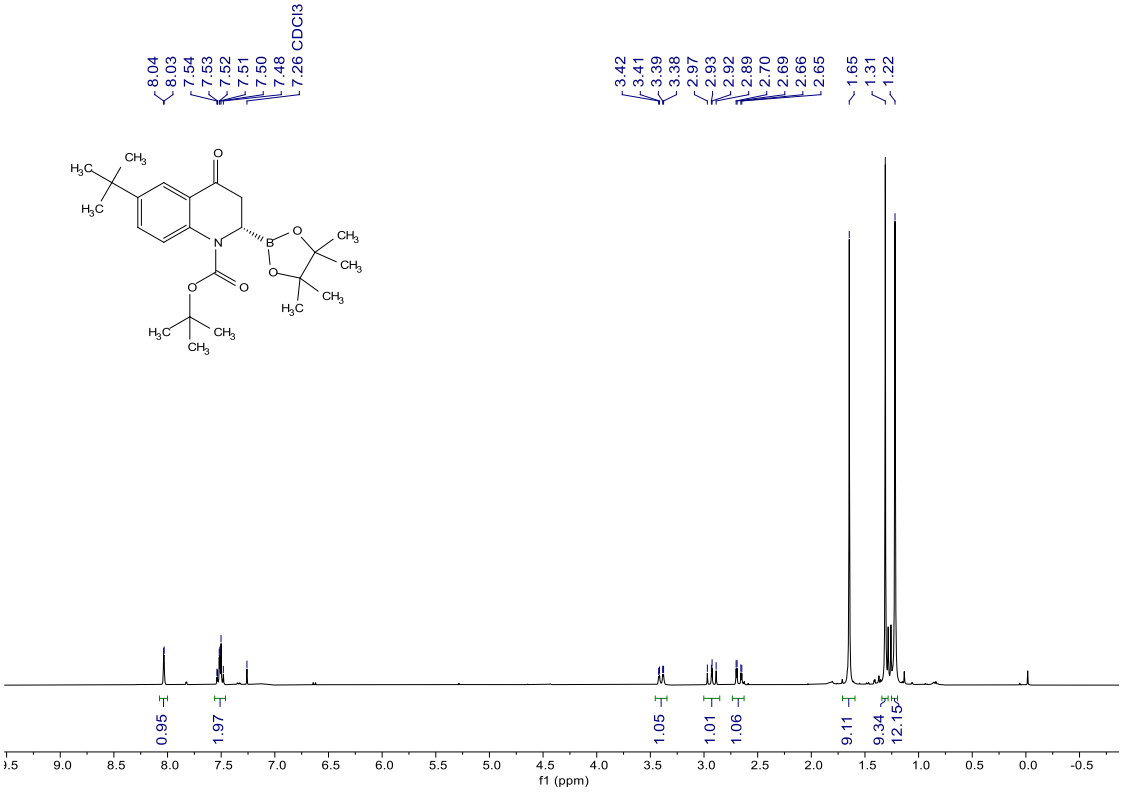


^{11}B NMR (128 MHz, $CDCl_3$)

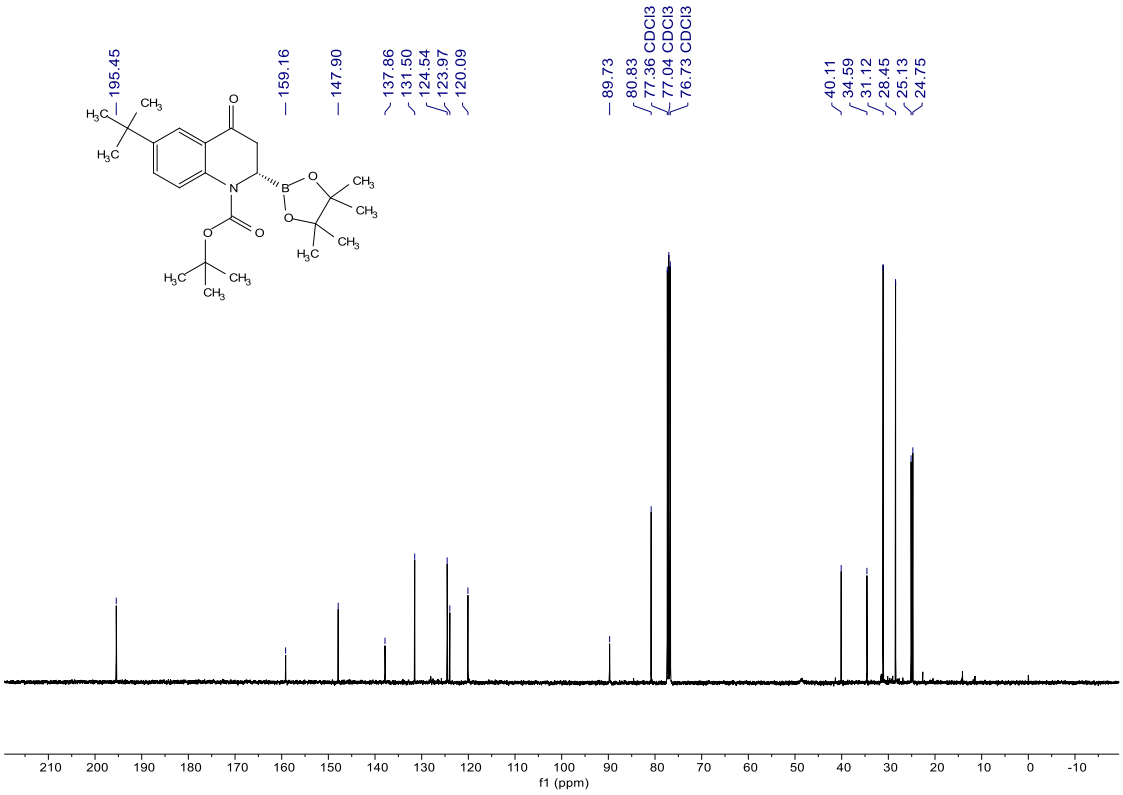


Compound 2e

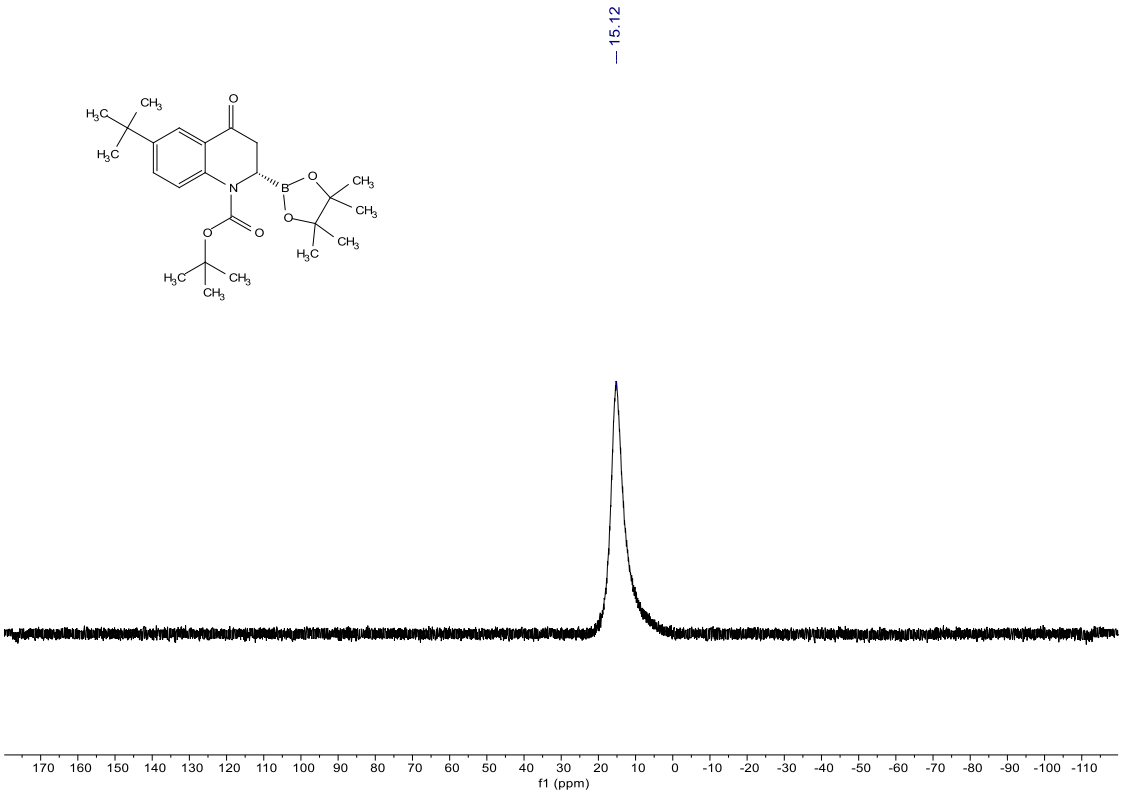
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

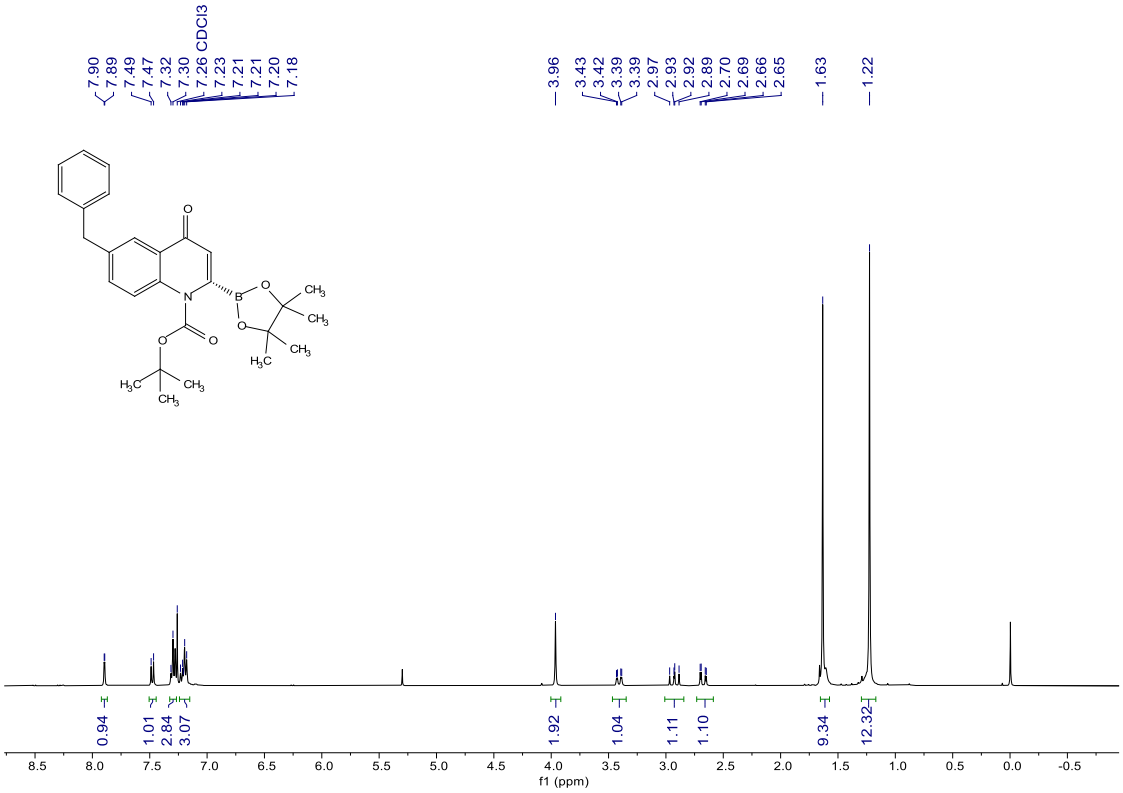


^{11}B NMR (128 MHz, $CDCl_3$)

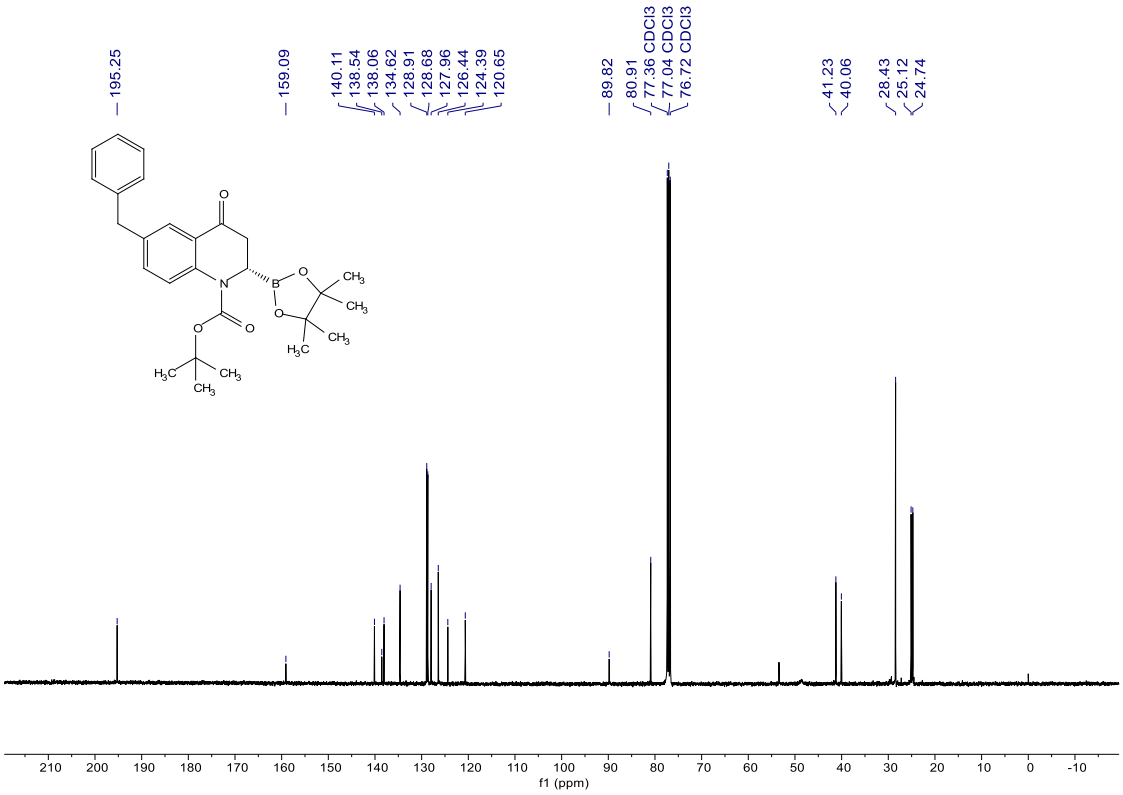


Compound 2f

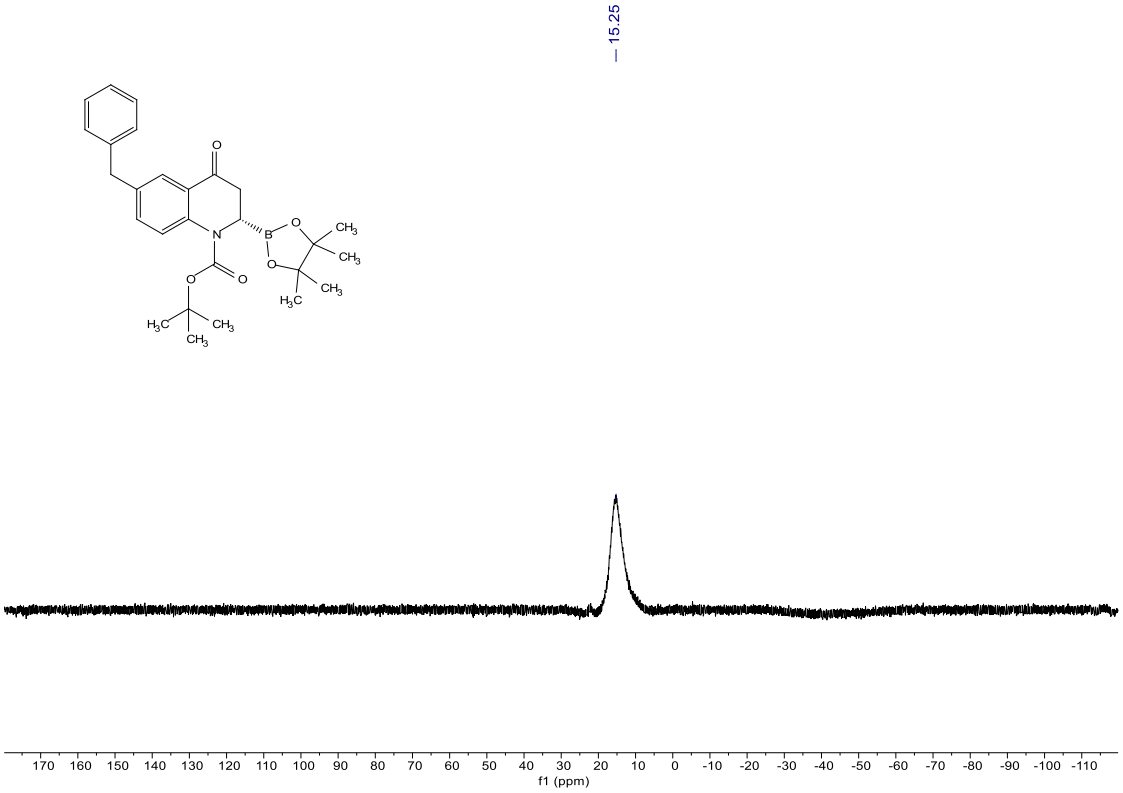
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

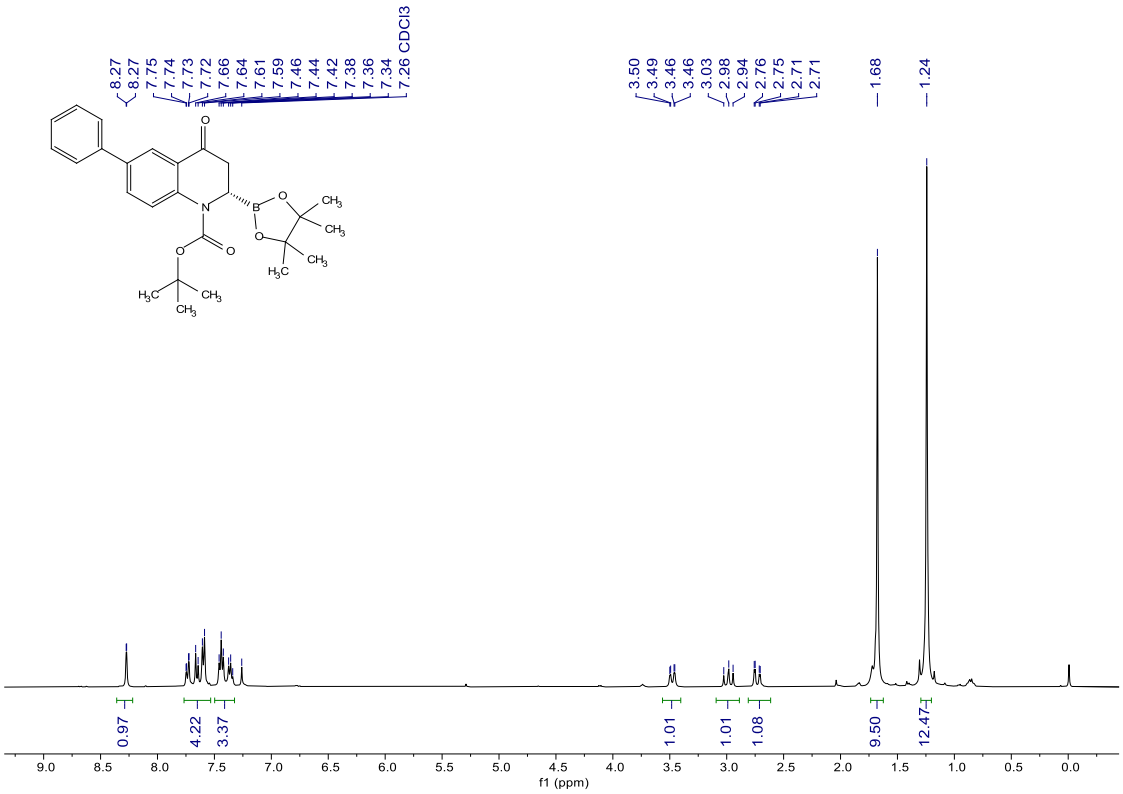


^{11}B NMR (128 MHz, $CDCl_3$)

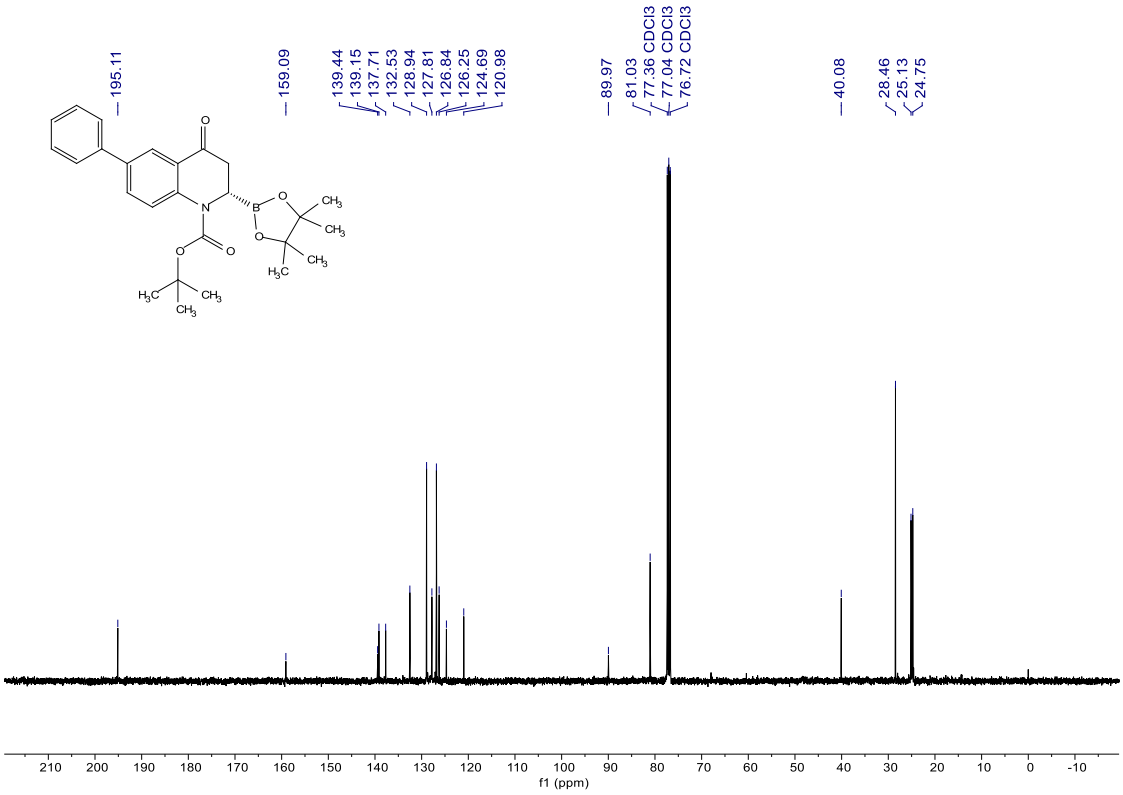


Compound 2g

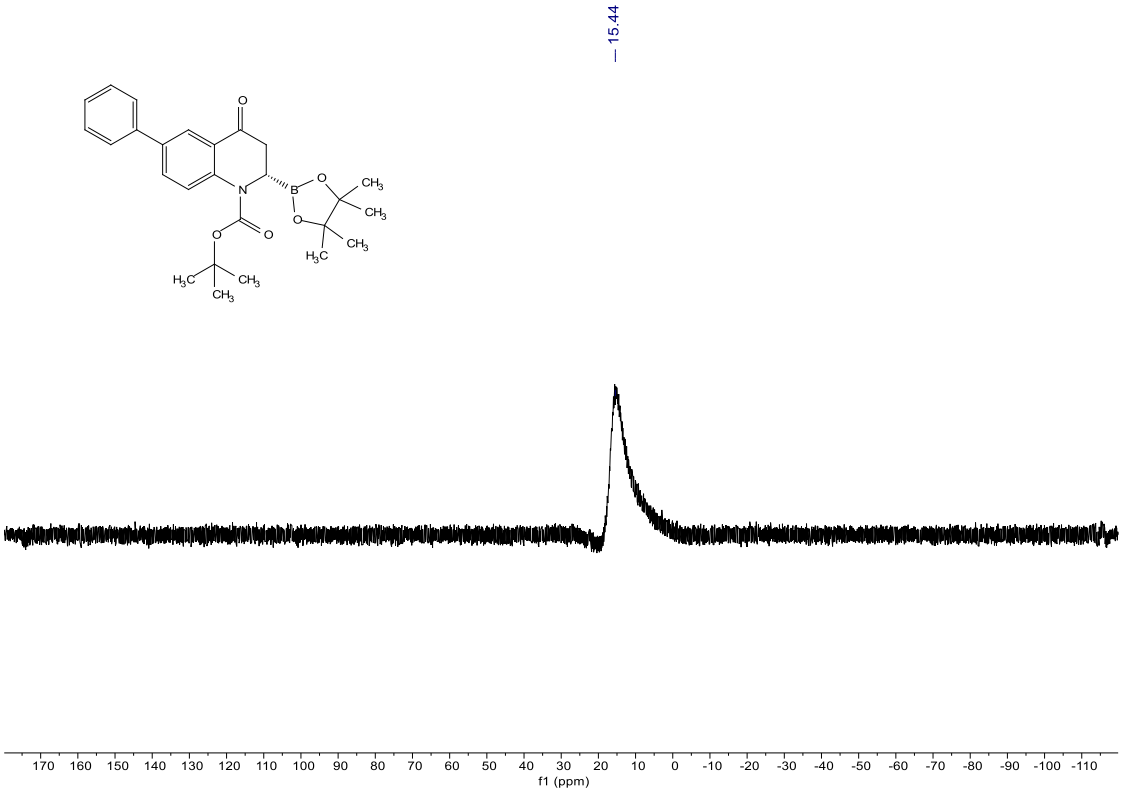
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

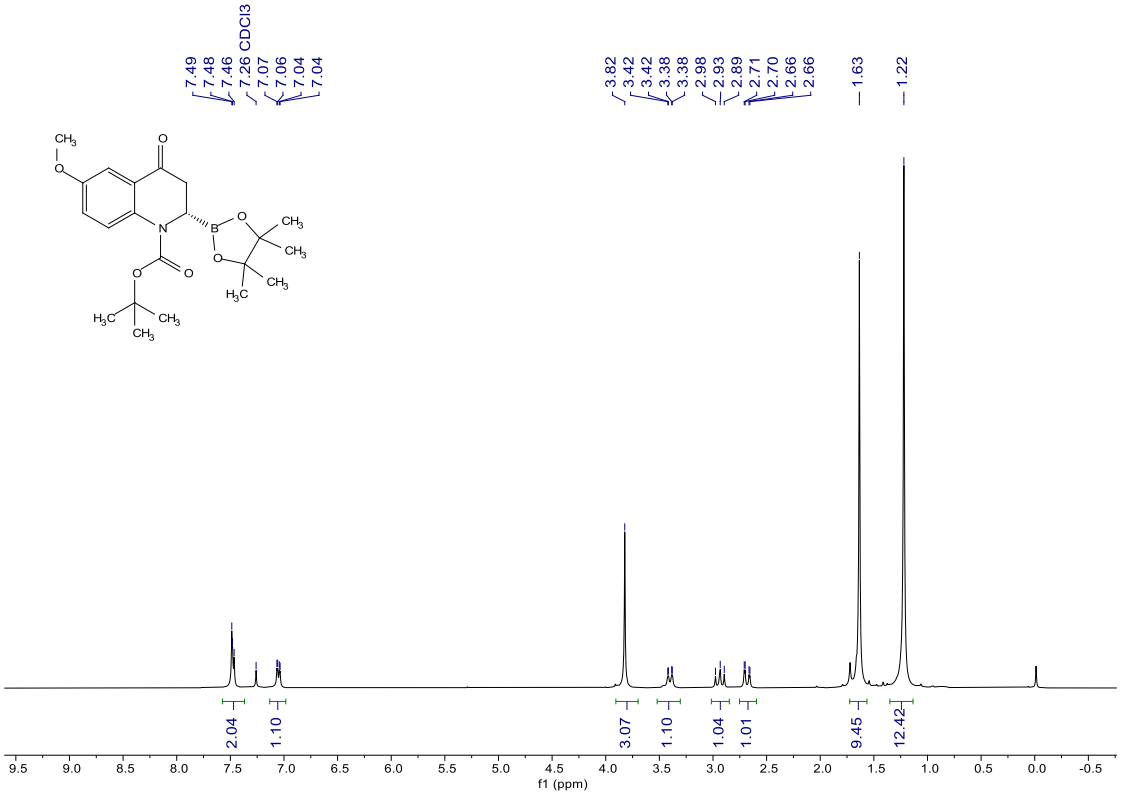


^{11}B NMR (128 MHz, $CDCl_3$)

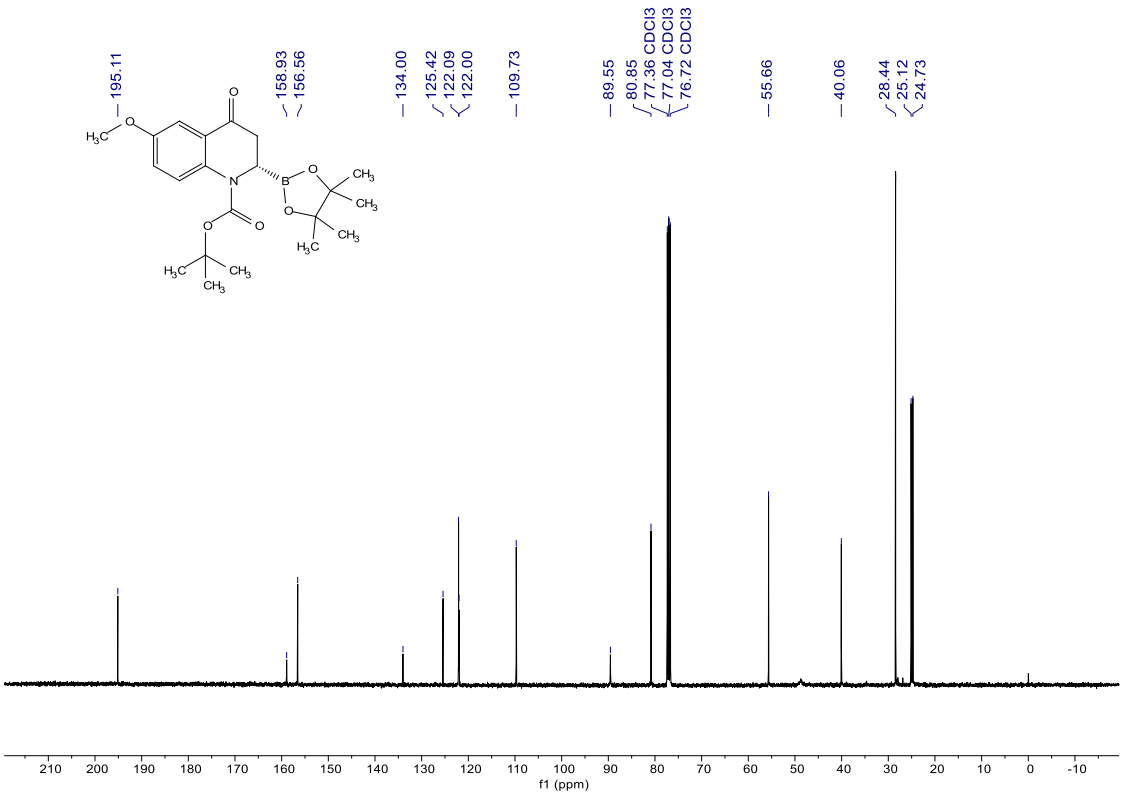


Compound 2h

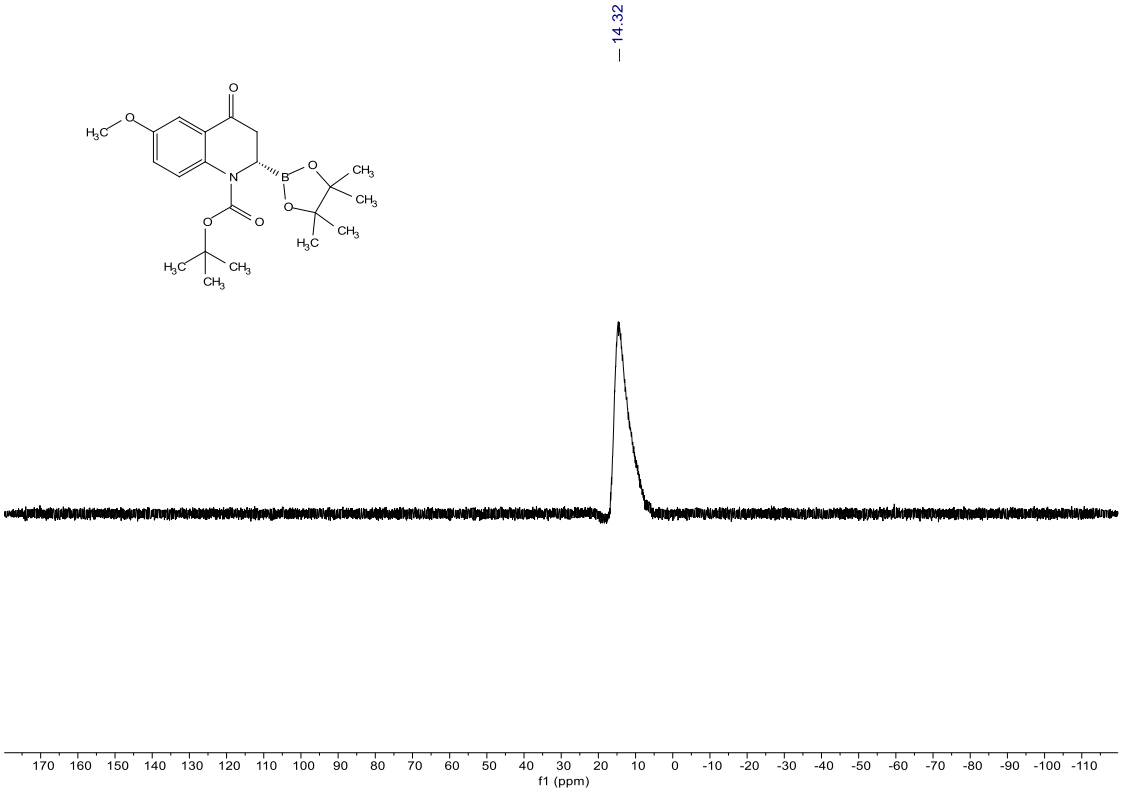
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

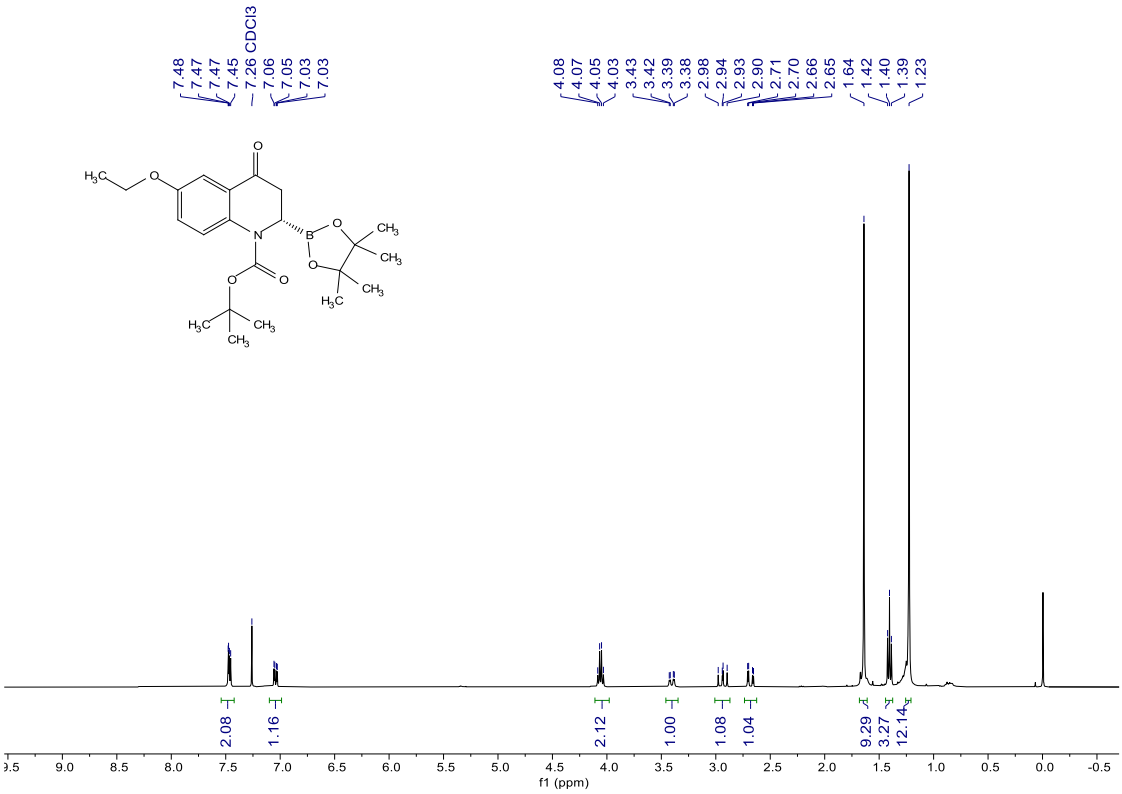


^{11}B NMR (128 MHz, $CDCl_3$)

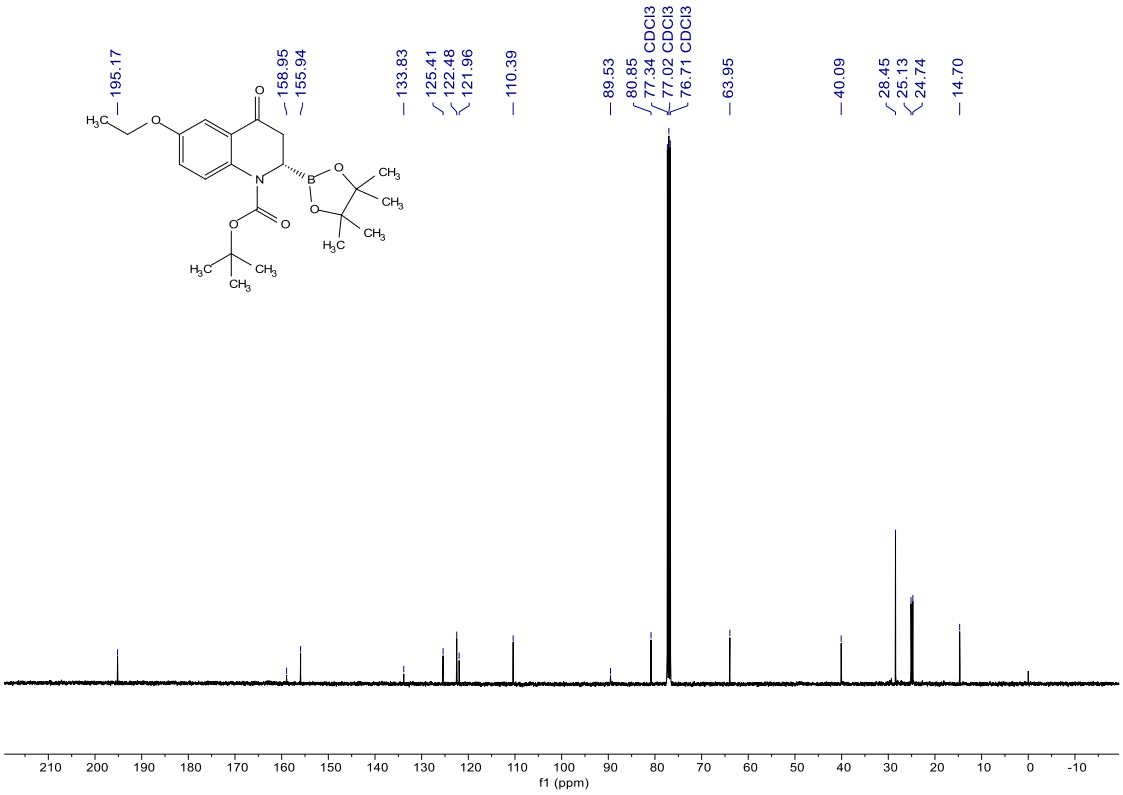


Compound 2i

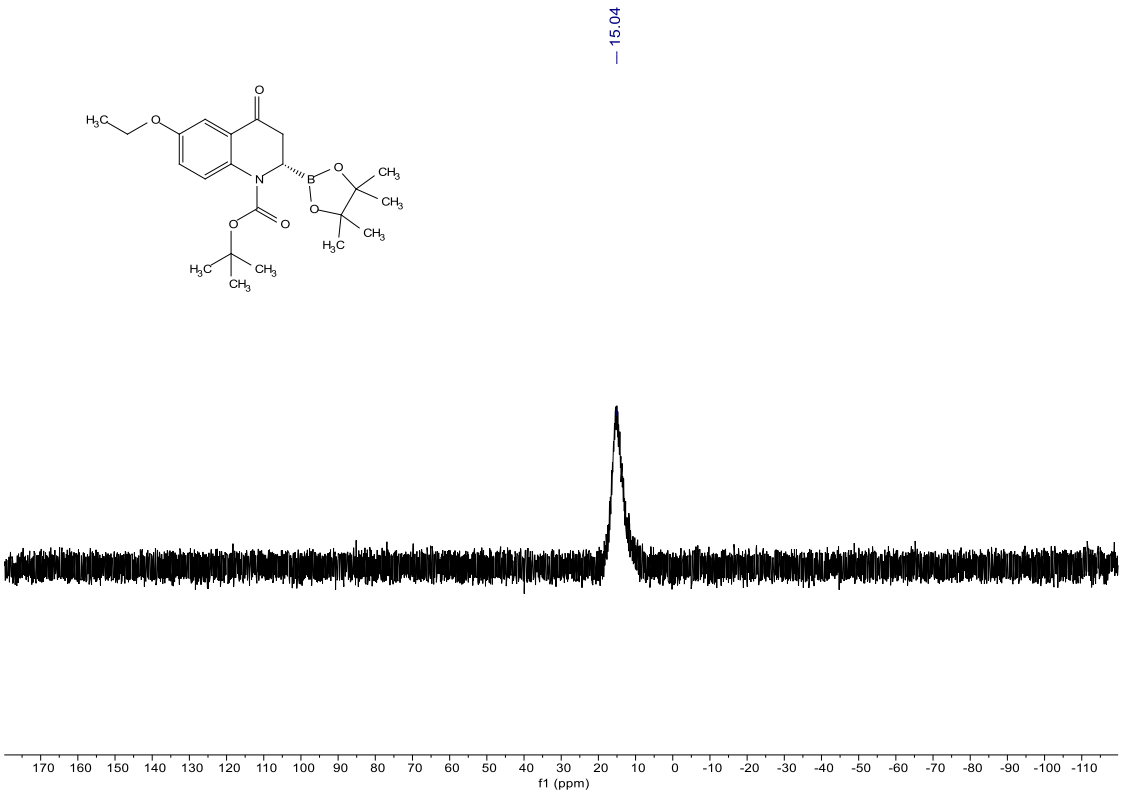
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

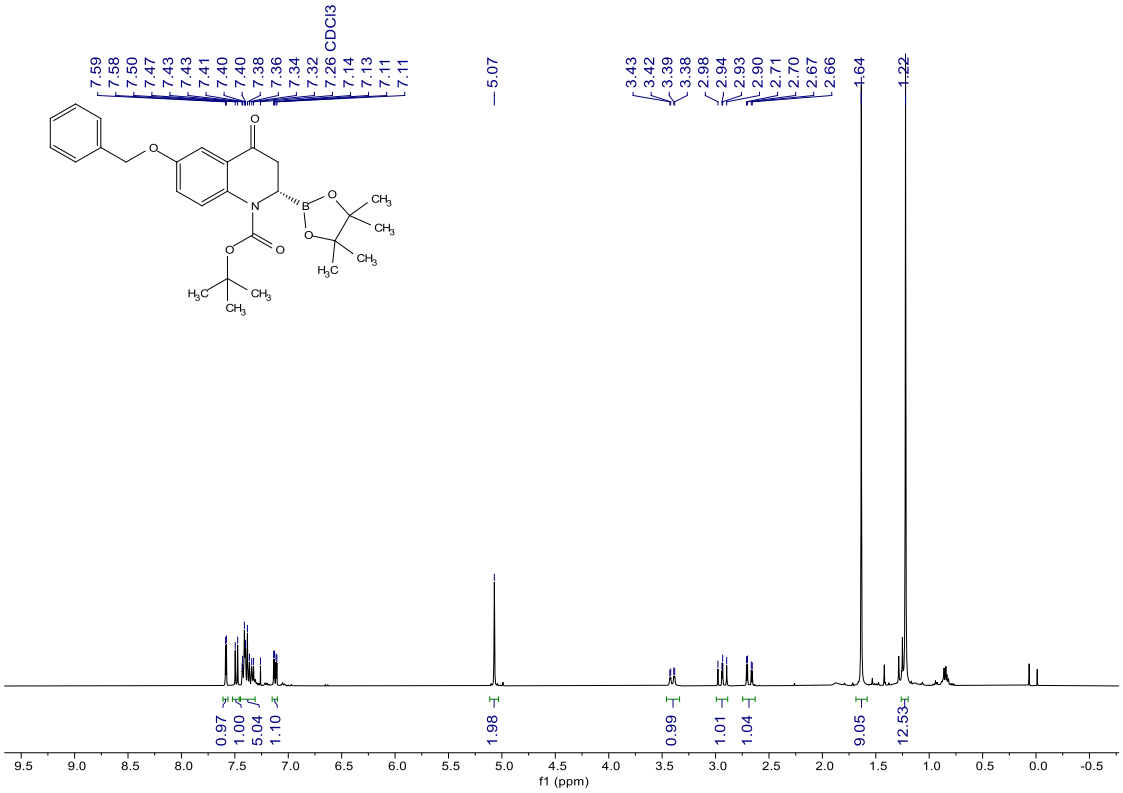


^{11}B NMR (128 MHz, $CDCl_3$)

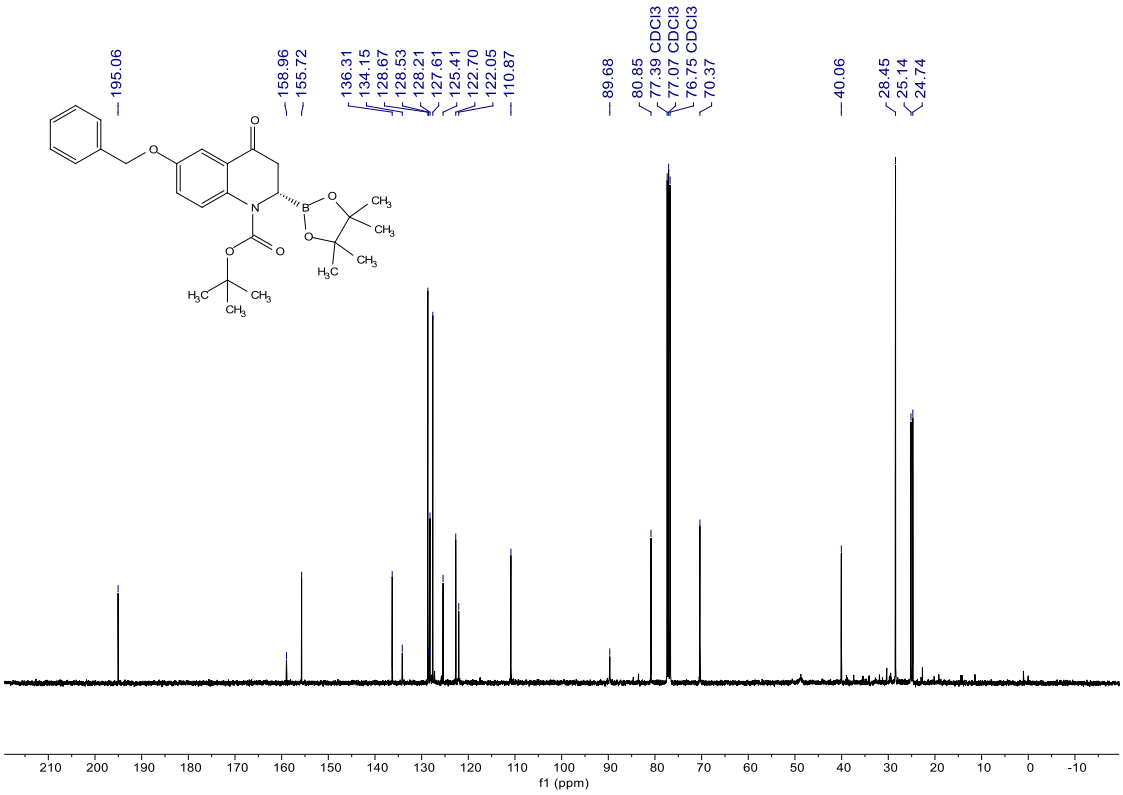


Compound 2j

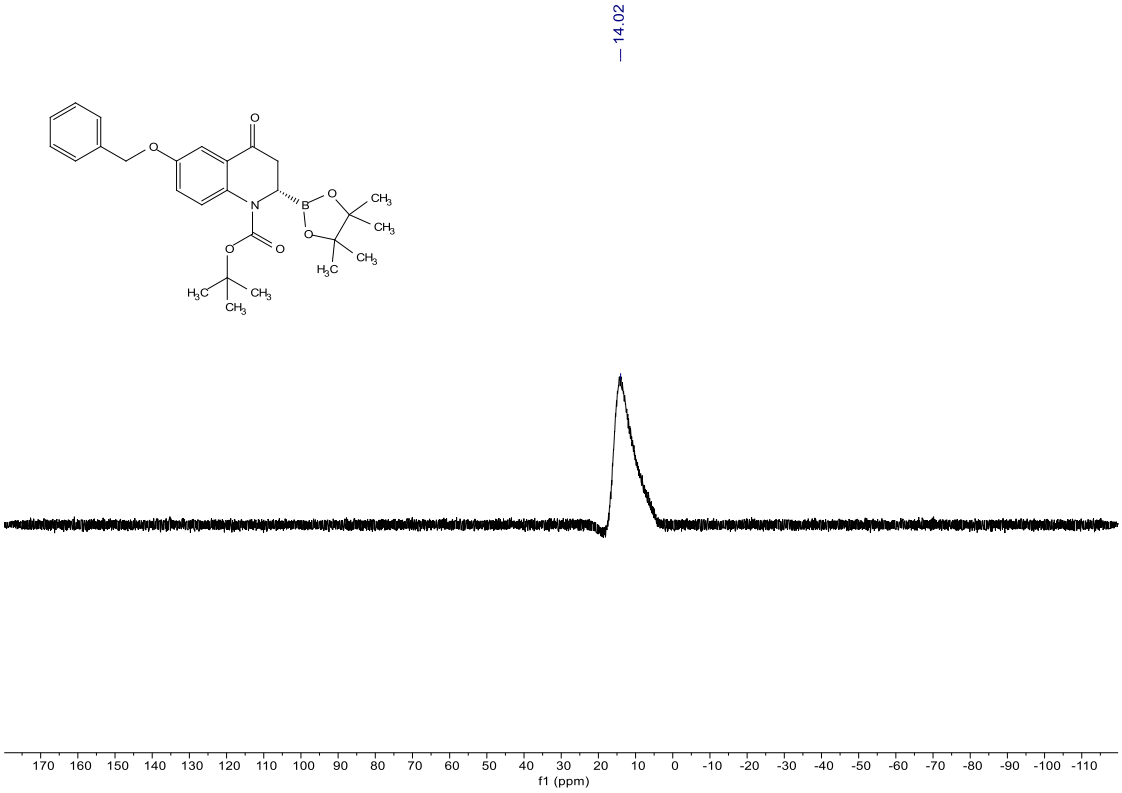
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

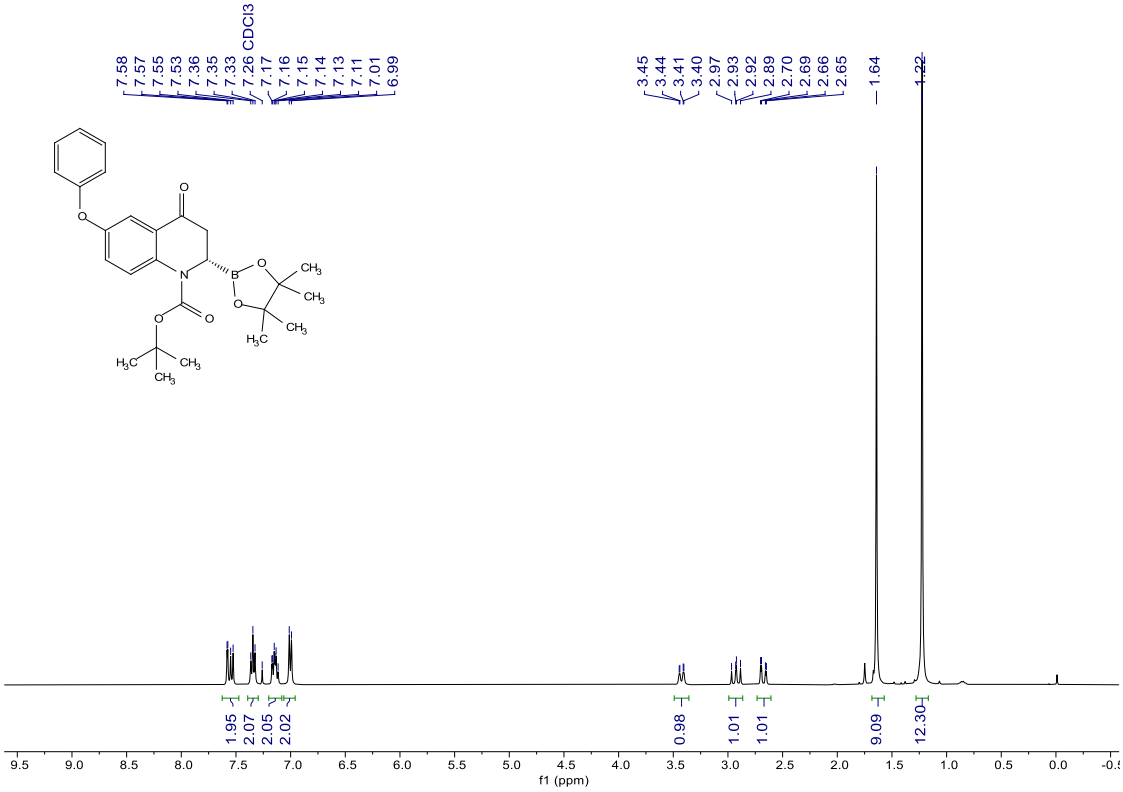


^{11}B NMR (128 MHz, $CDCl_3$)

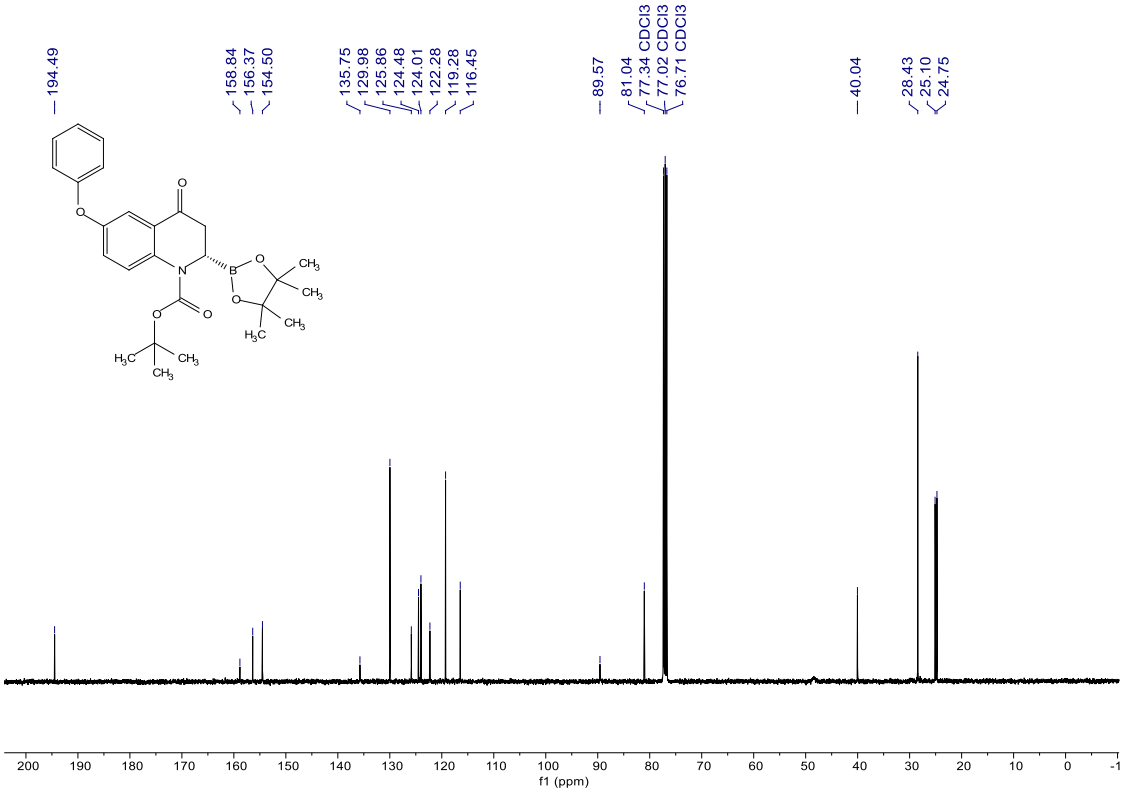


Compound 2k

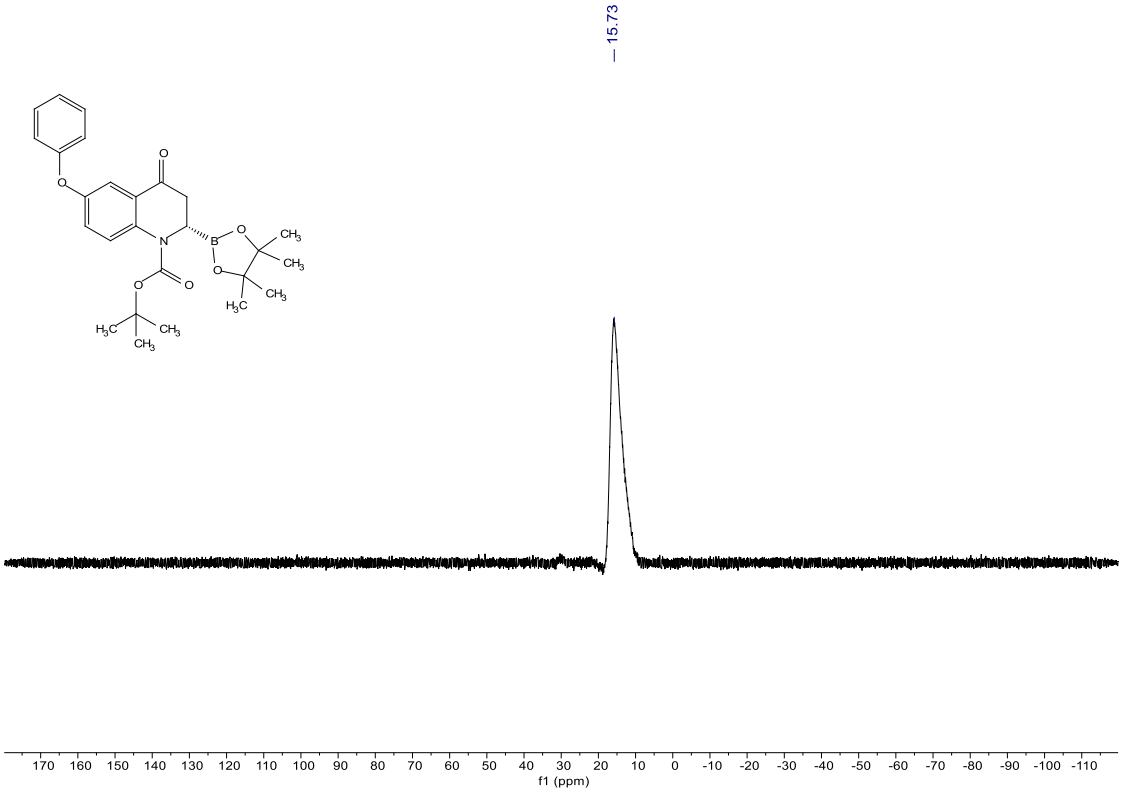
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

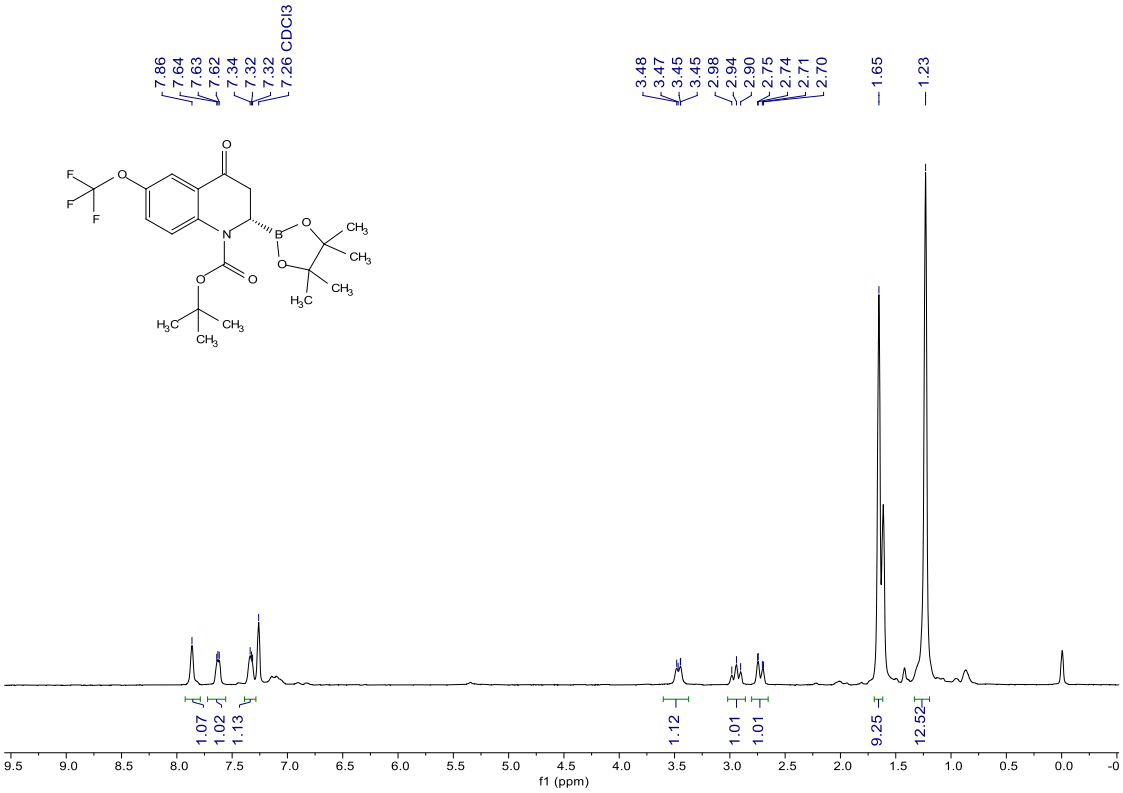


^{11}B NMR (128 MHz, $CDCl_3$)

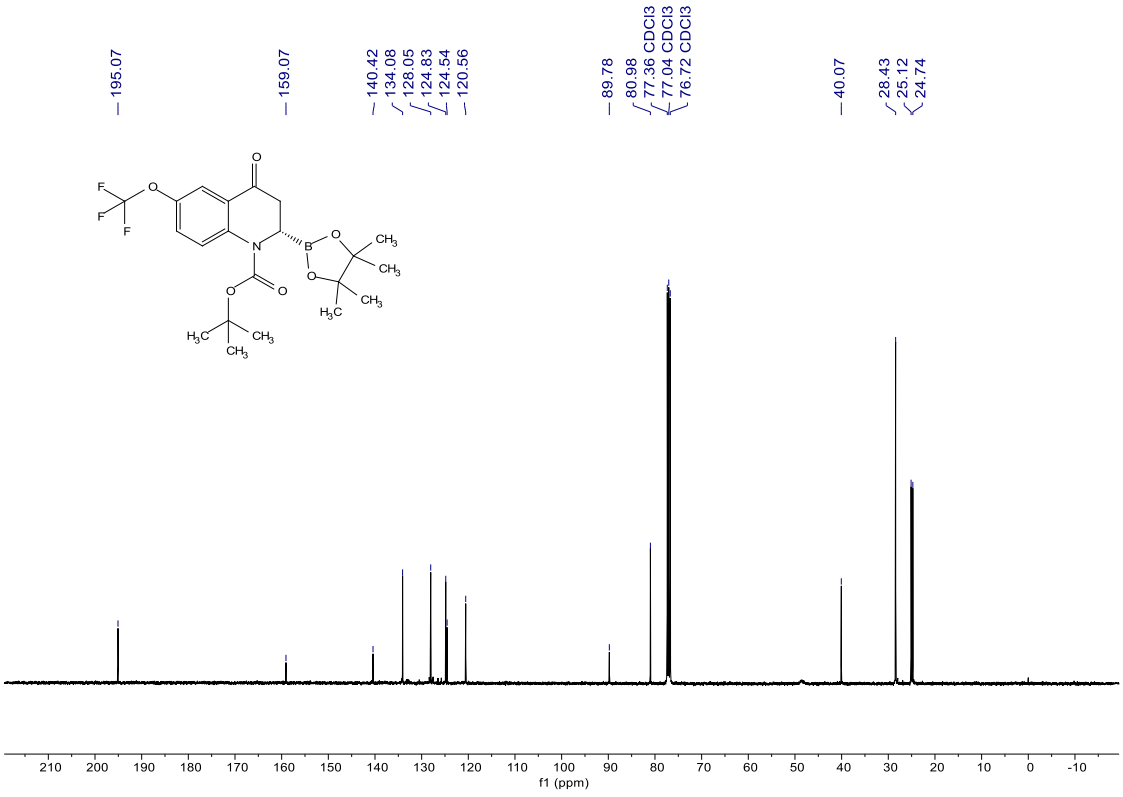


Compound 2l

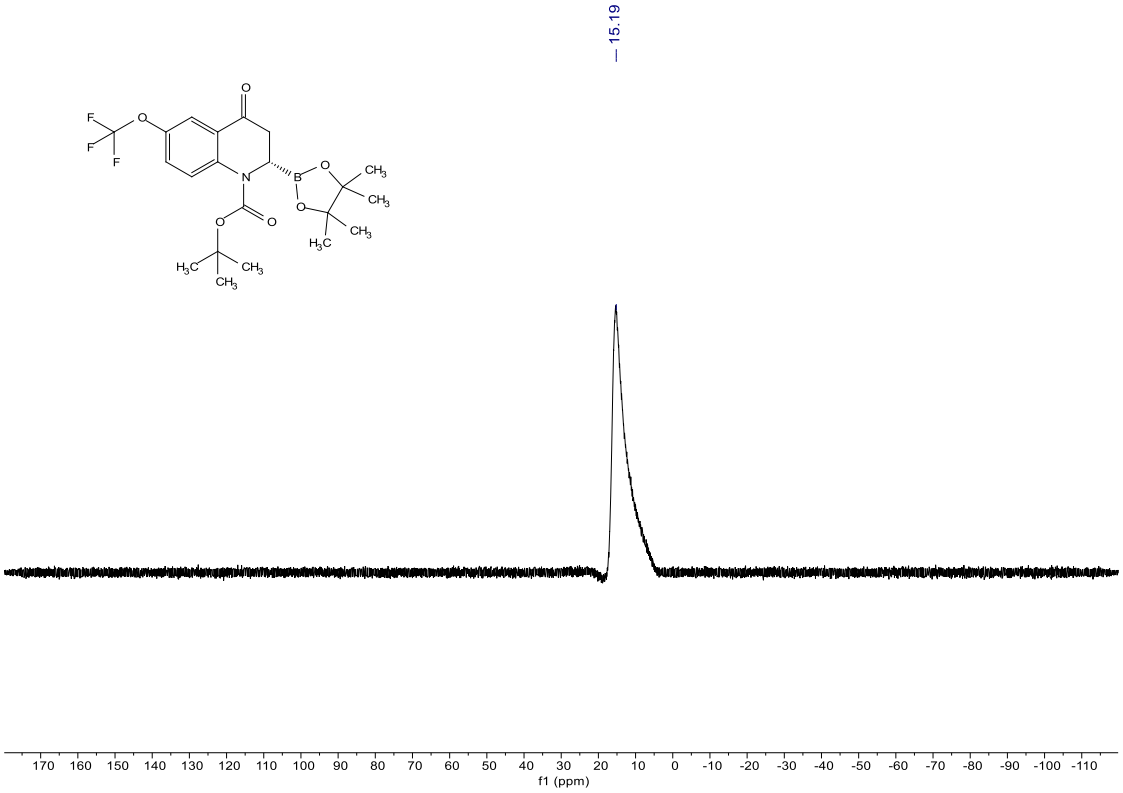
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

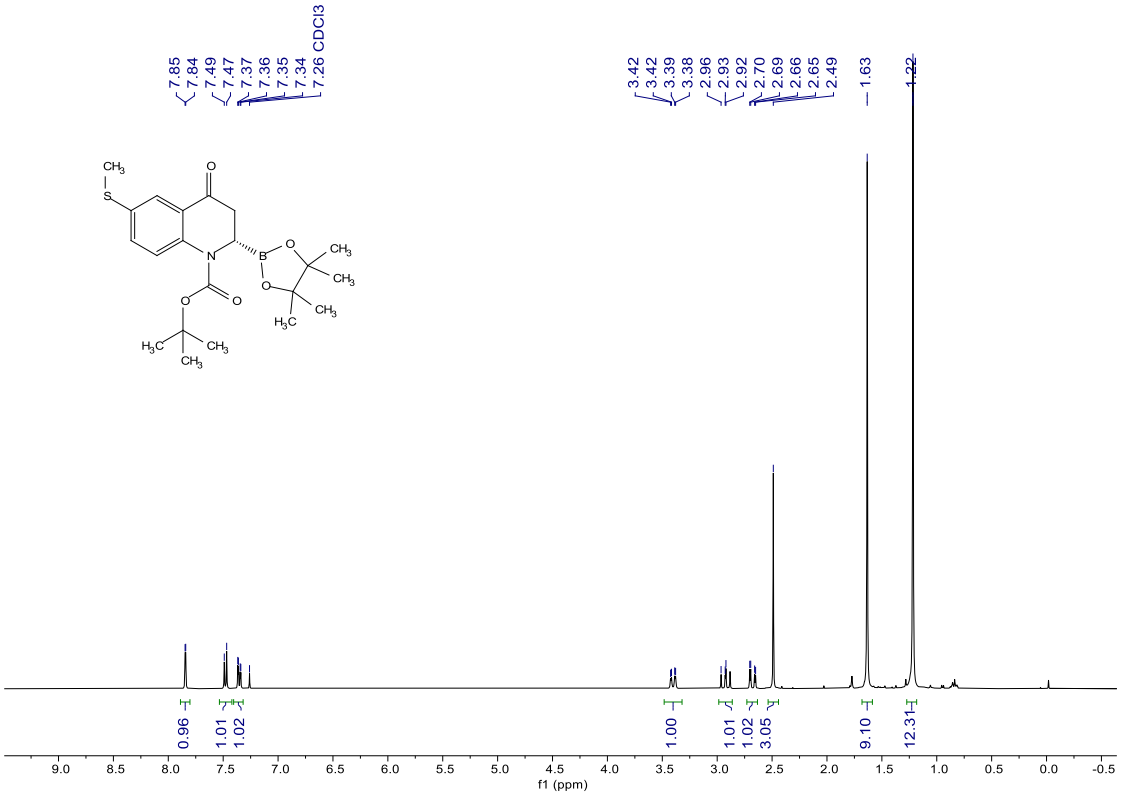


^{11}B NMR (128 MHz, $CDCl_3$)

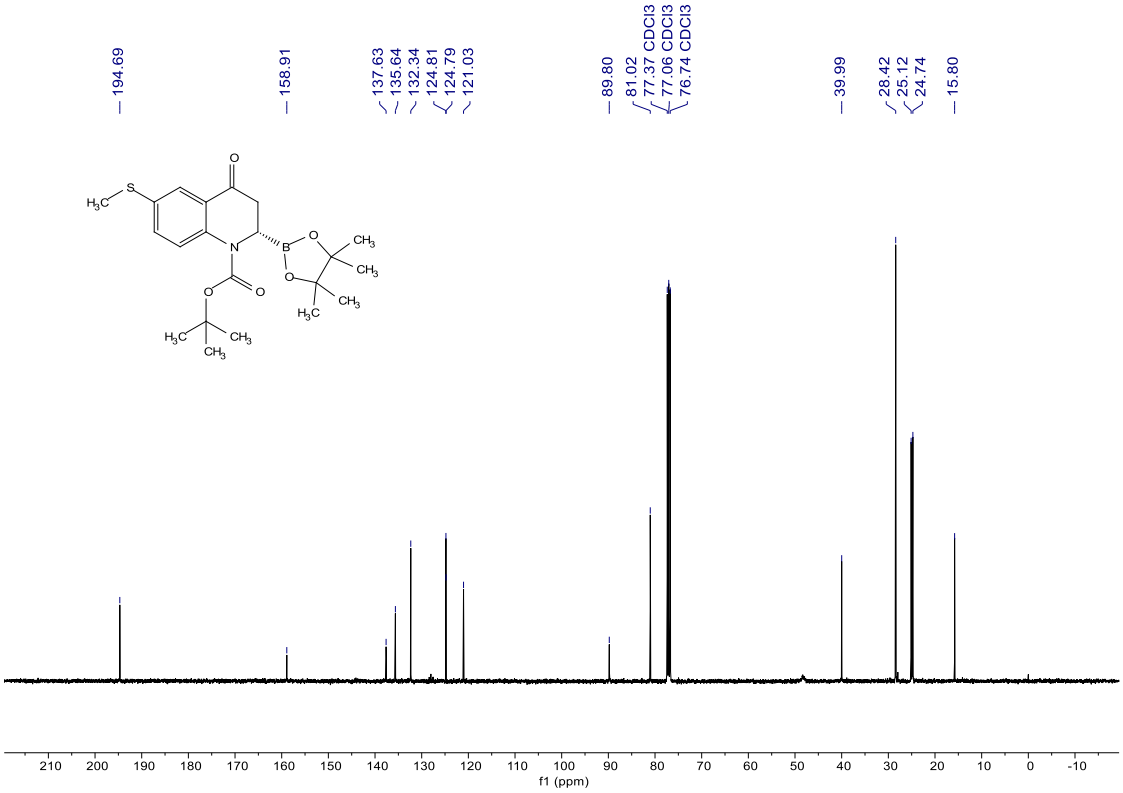


Compound 2m

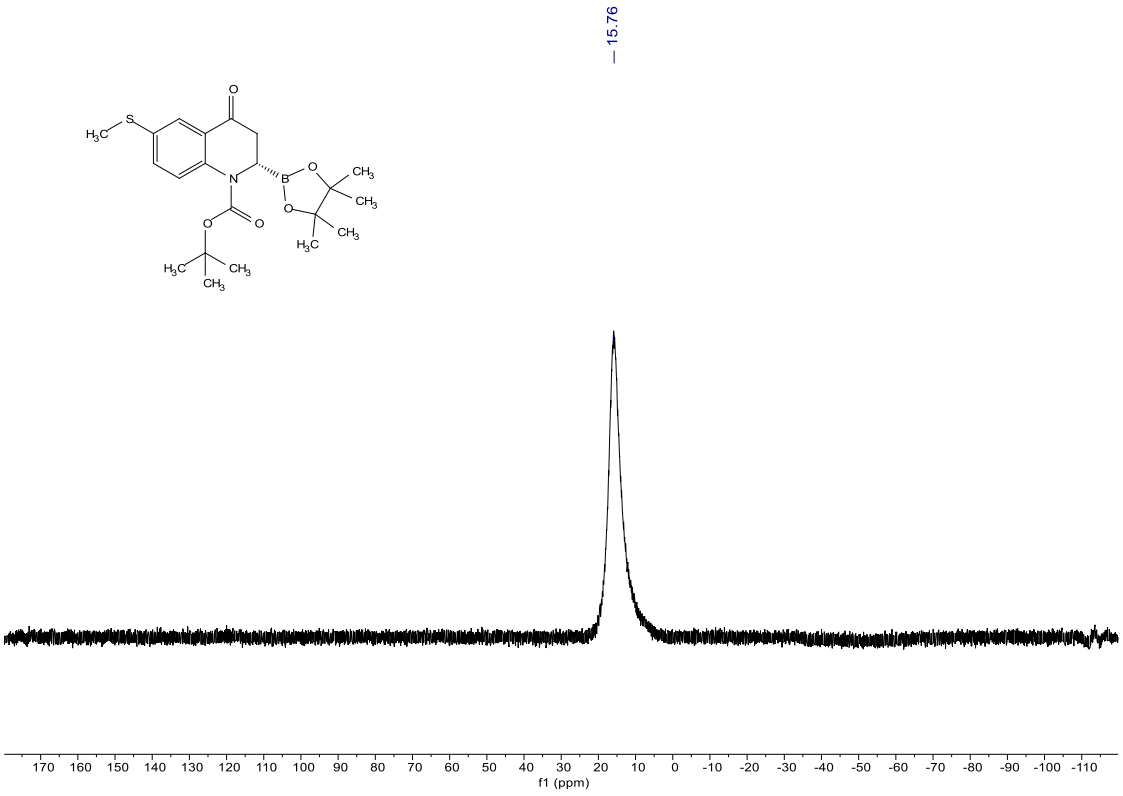
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

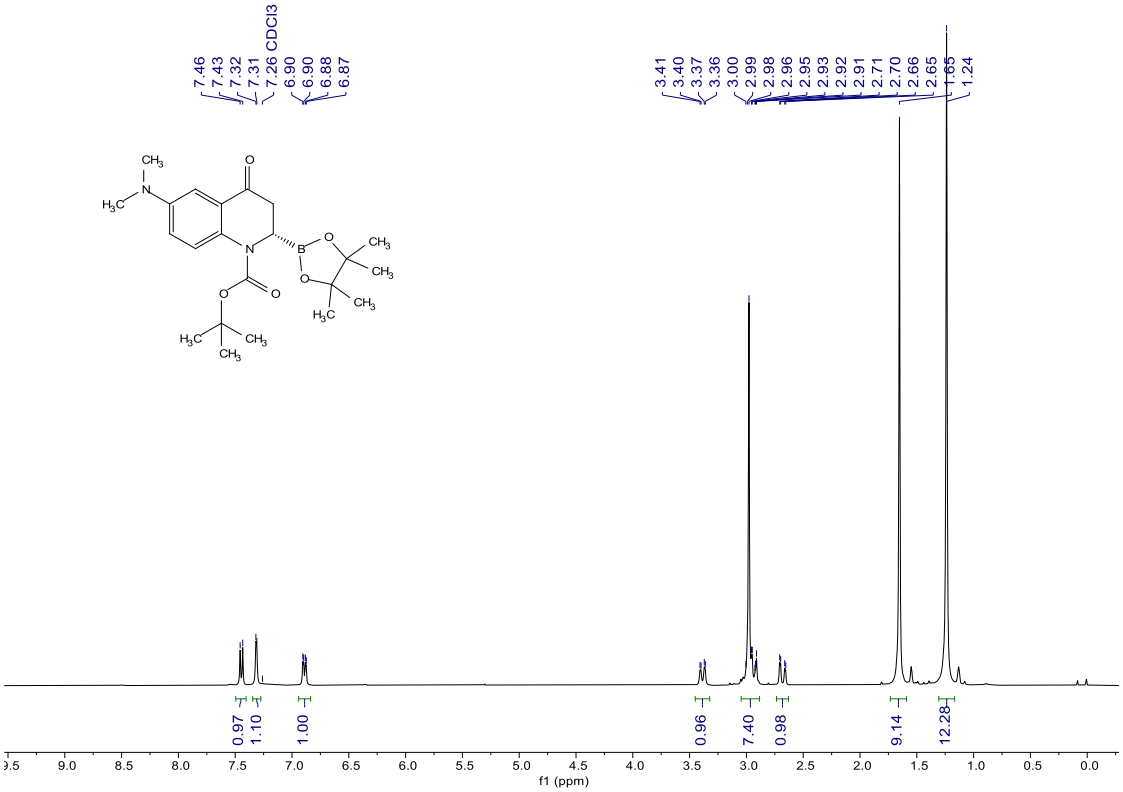


^{11}B NMR (128 MHz, $CDCl_3$)

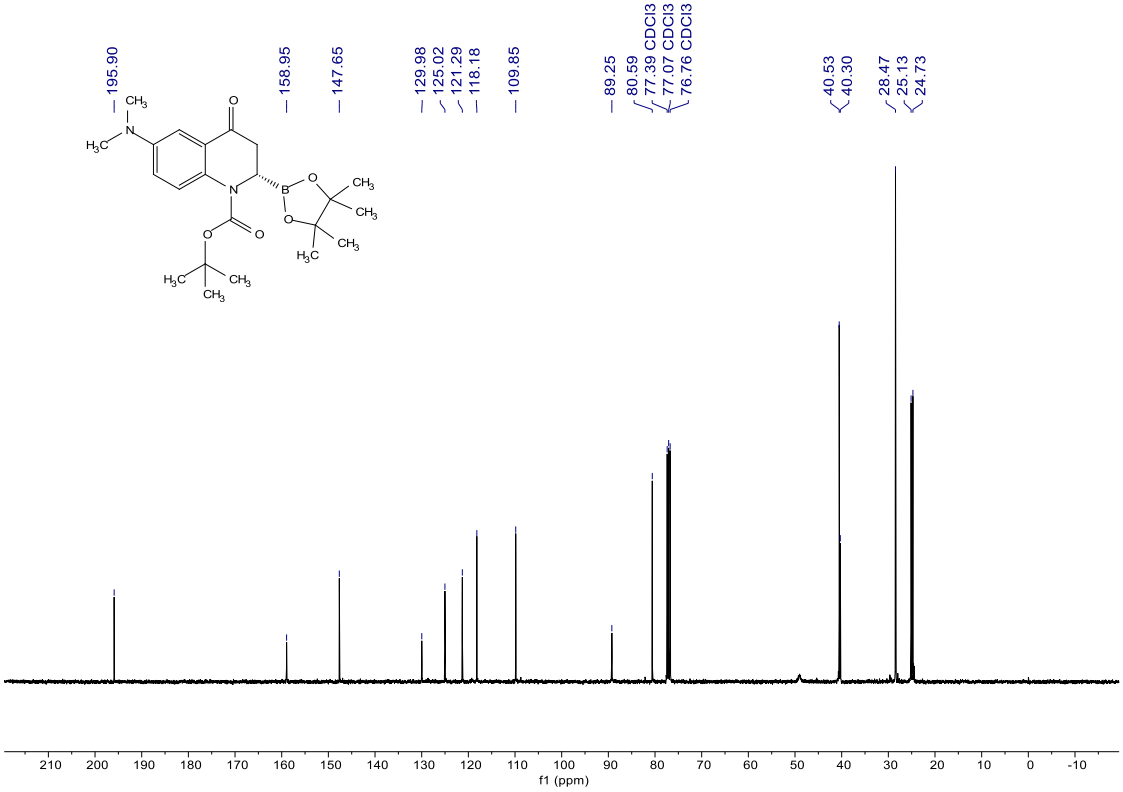


Compound 2n

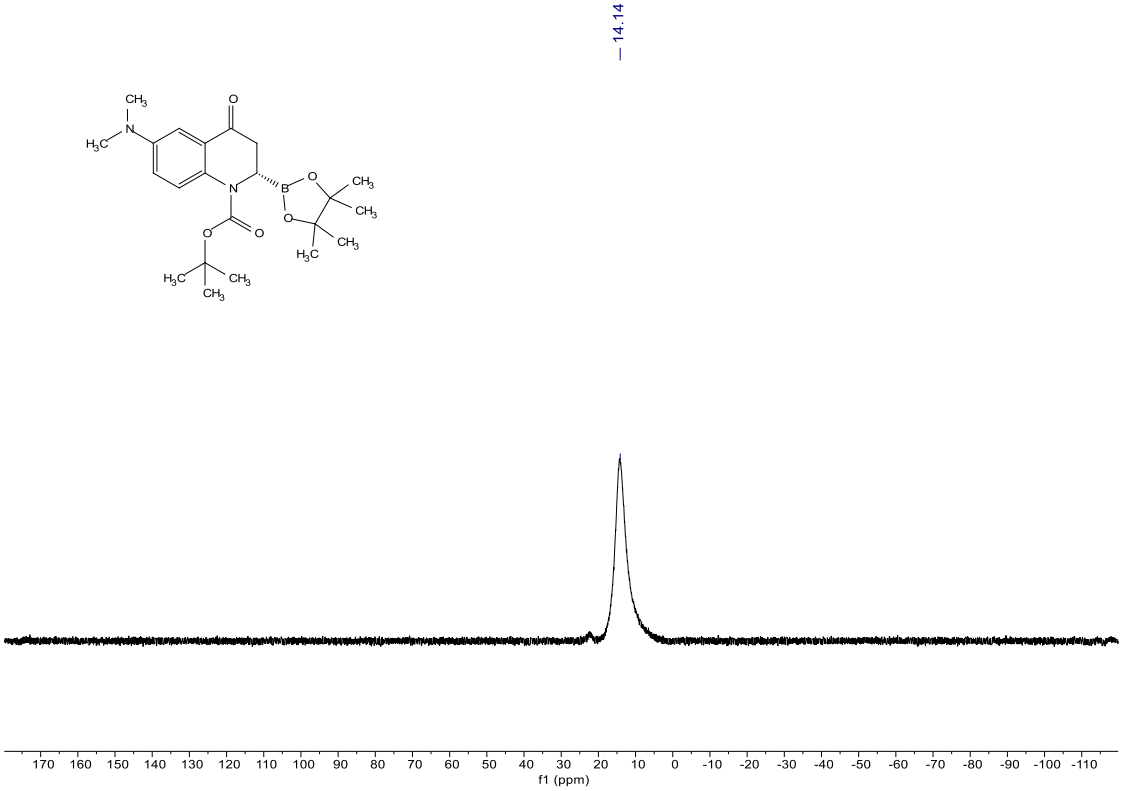
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

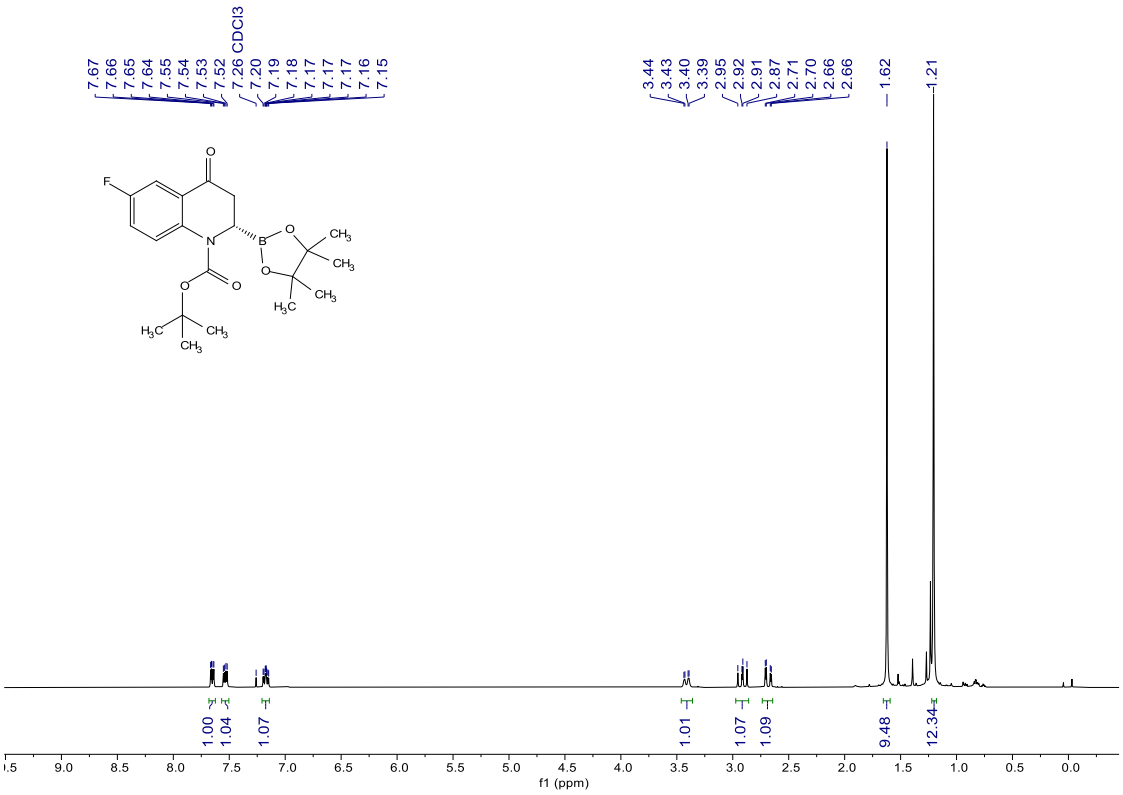


^{11}B NMR (128 MHz, $CDCl_3$)

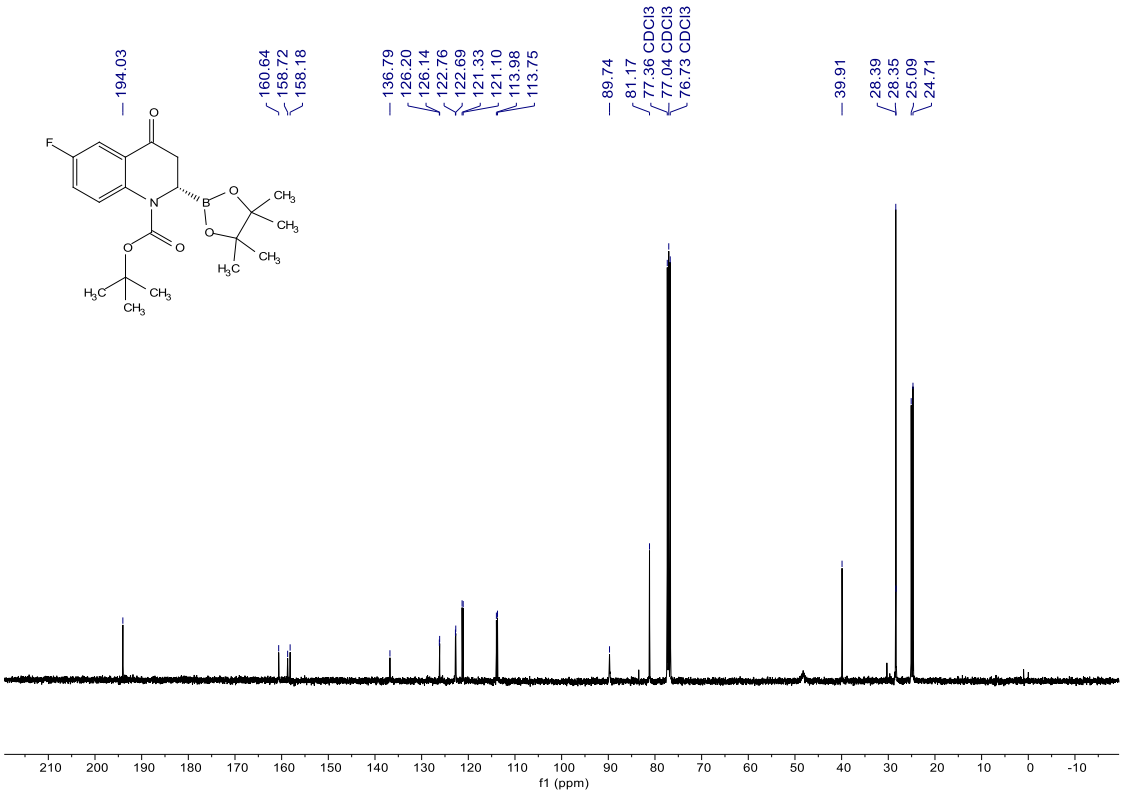


Compound 2o

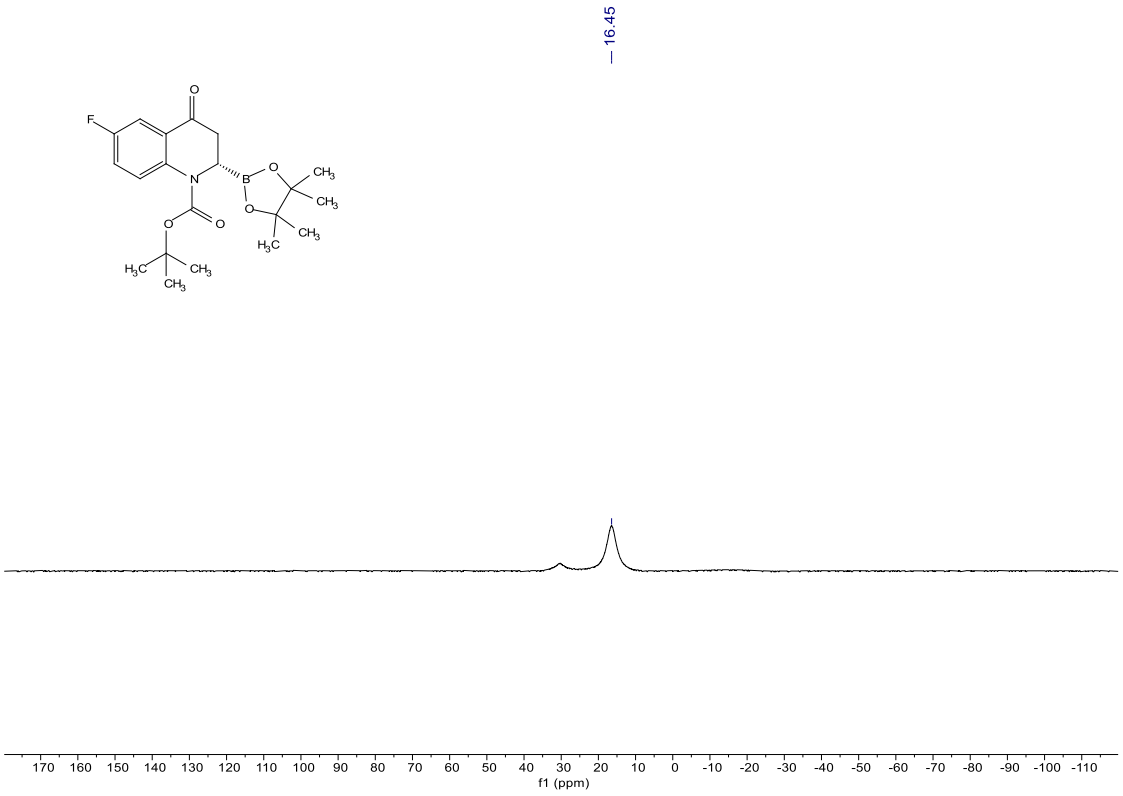
^{1}H NMR (400 MHz, $CDCl_3$)



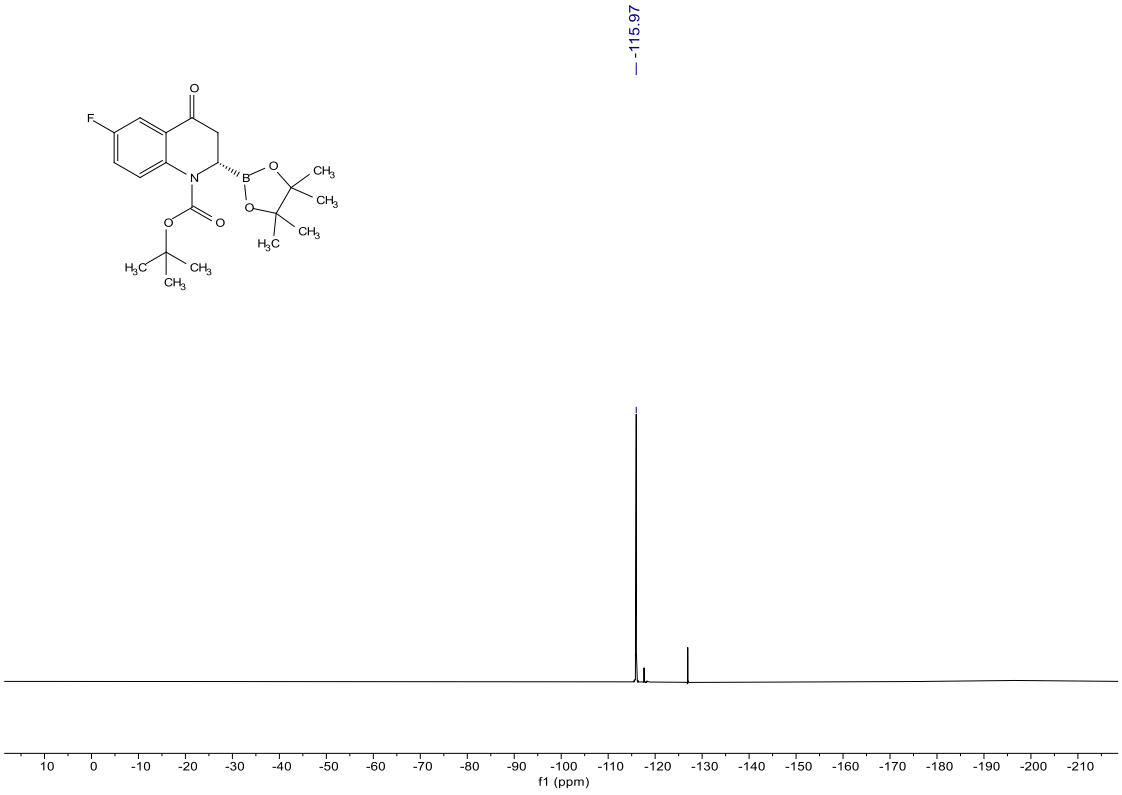
^{13}C NMR (101 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, $CDCl_3$)

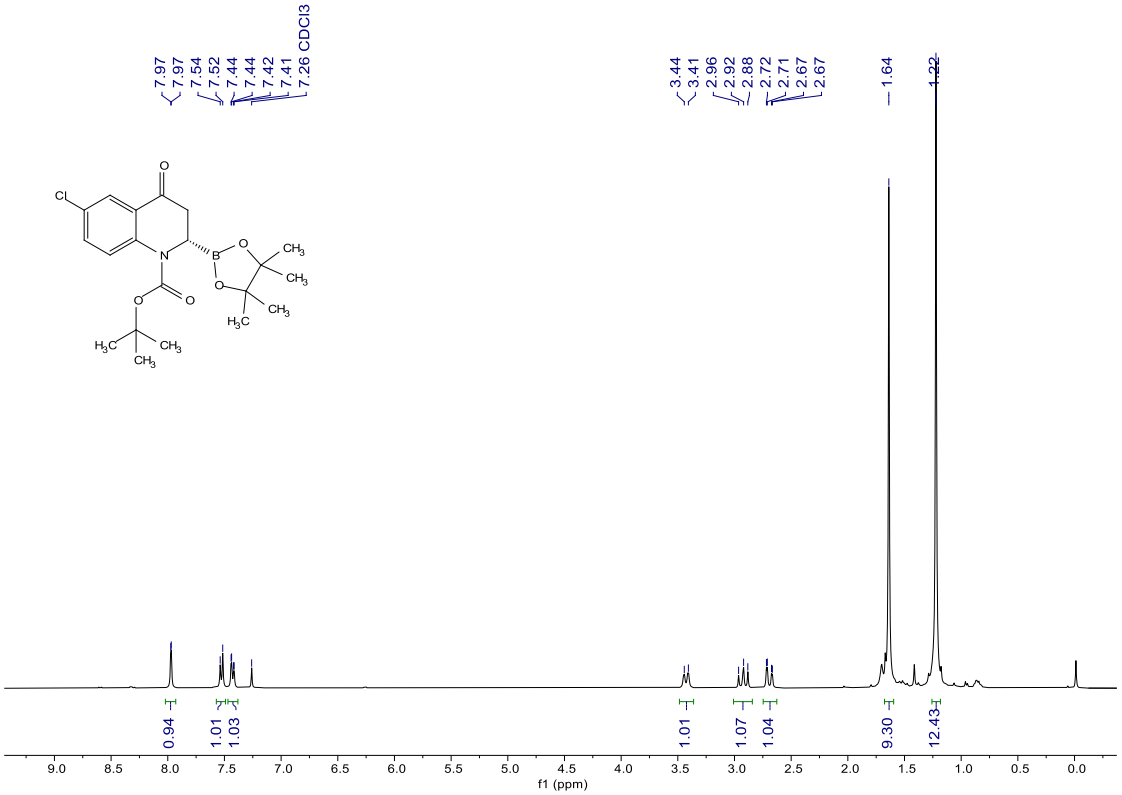


^{19}F NMR (376 MHz, $CDCl_3$)

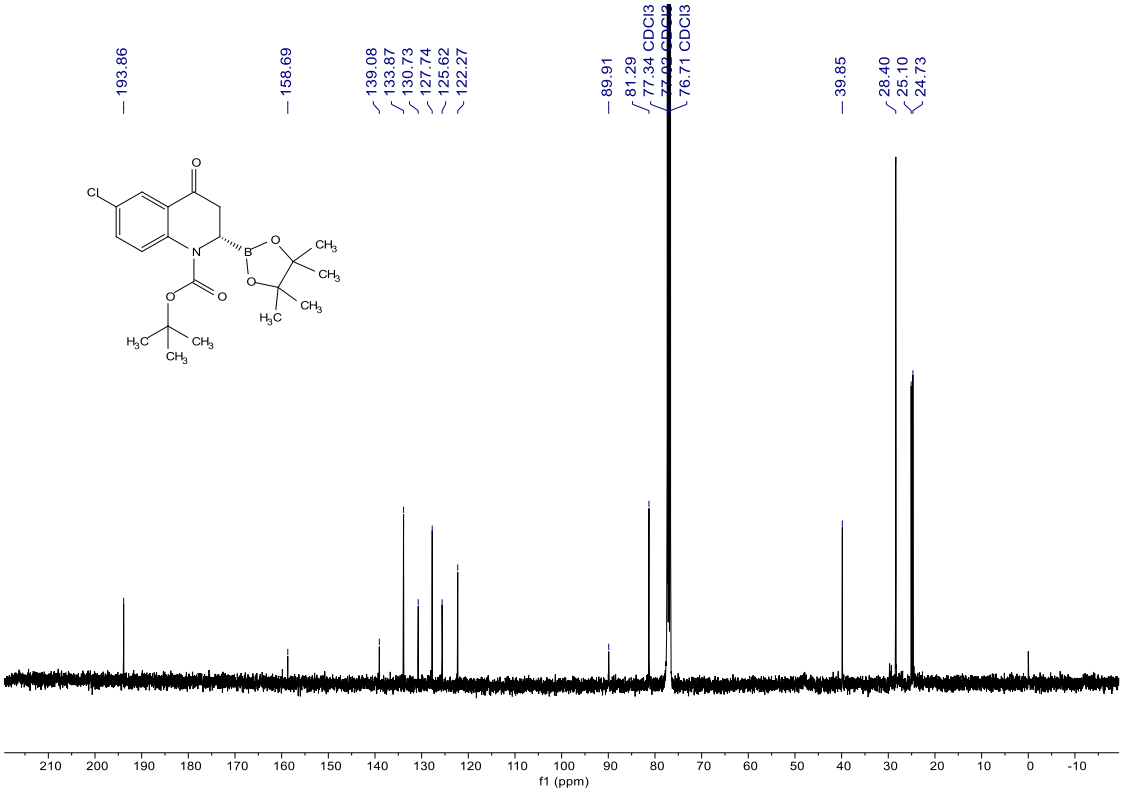


Compound 2p

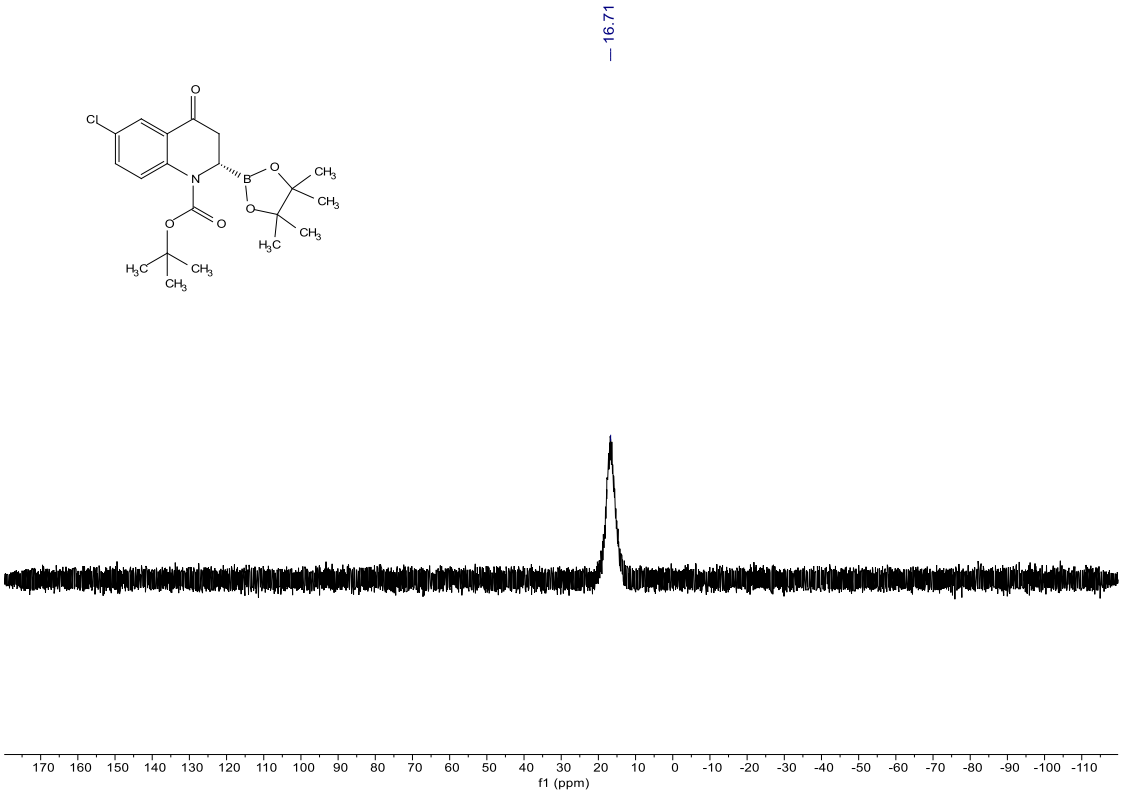
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

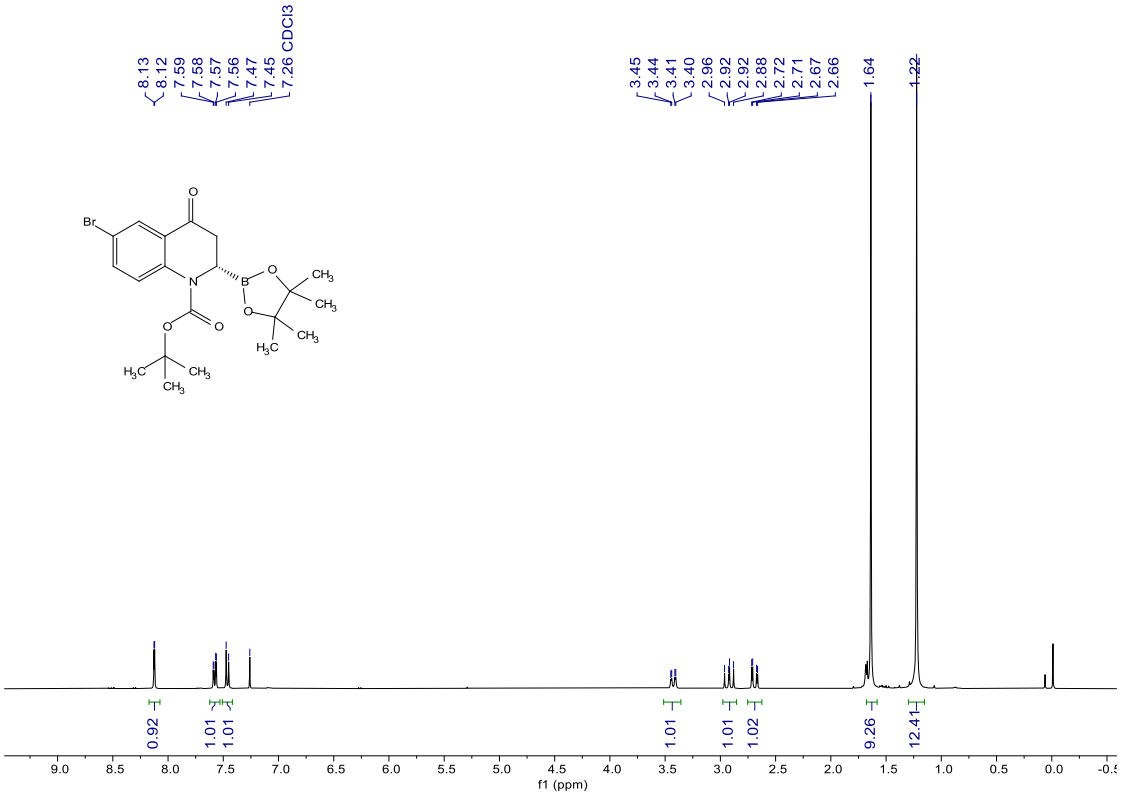


^{11}B NMR (128 MHz, $CDCl_3$)

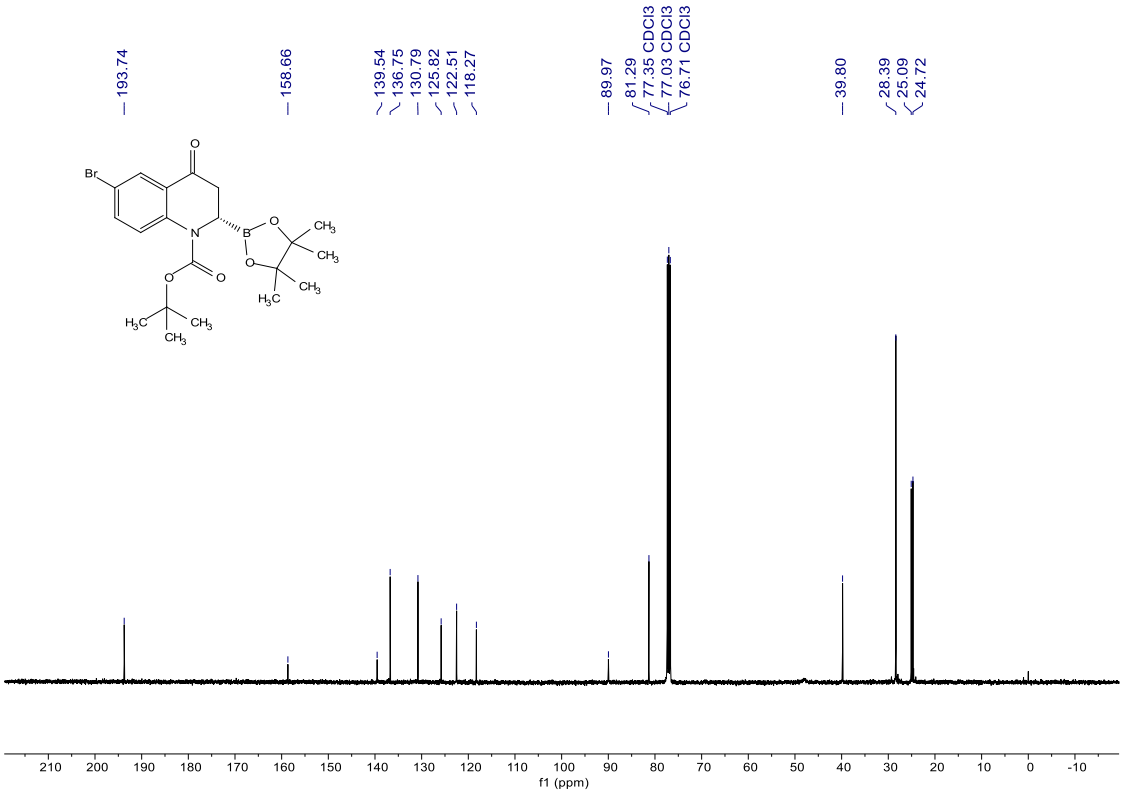


Compound 2q

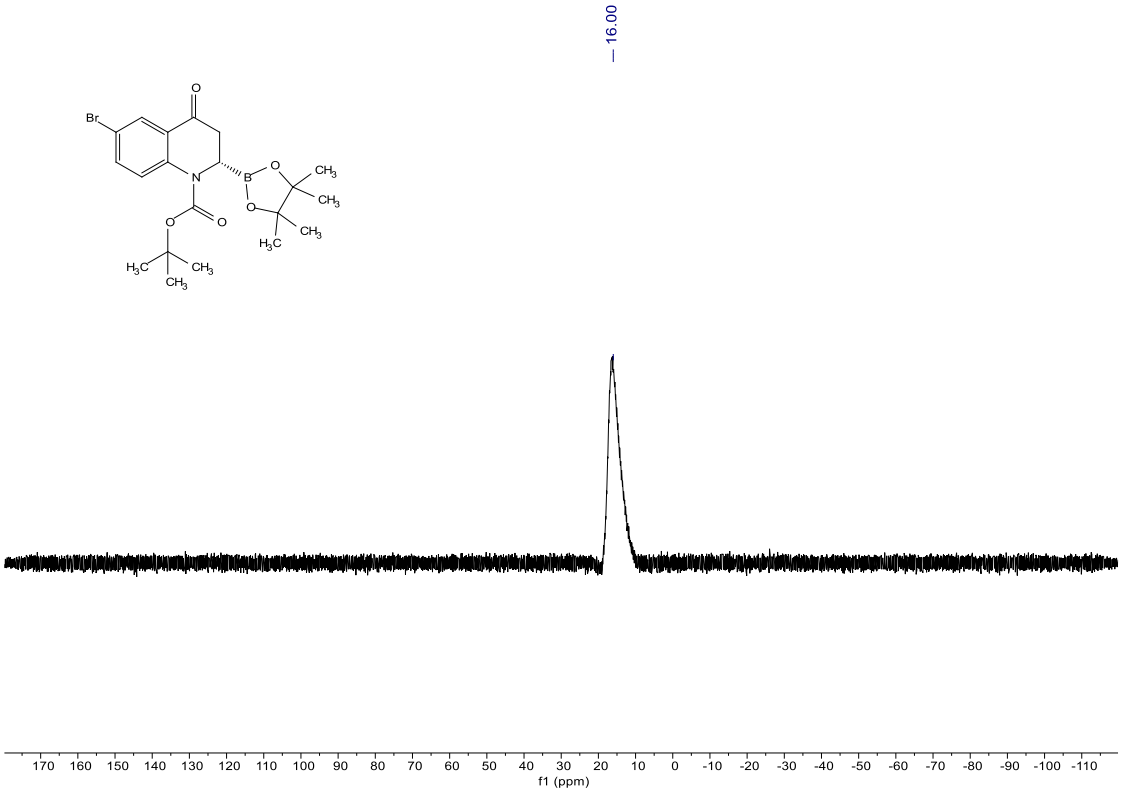
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

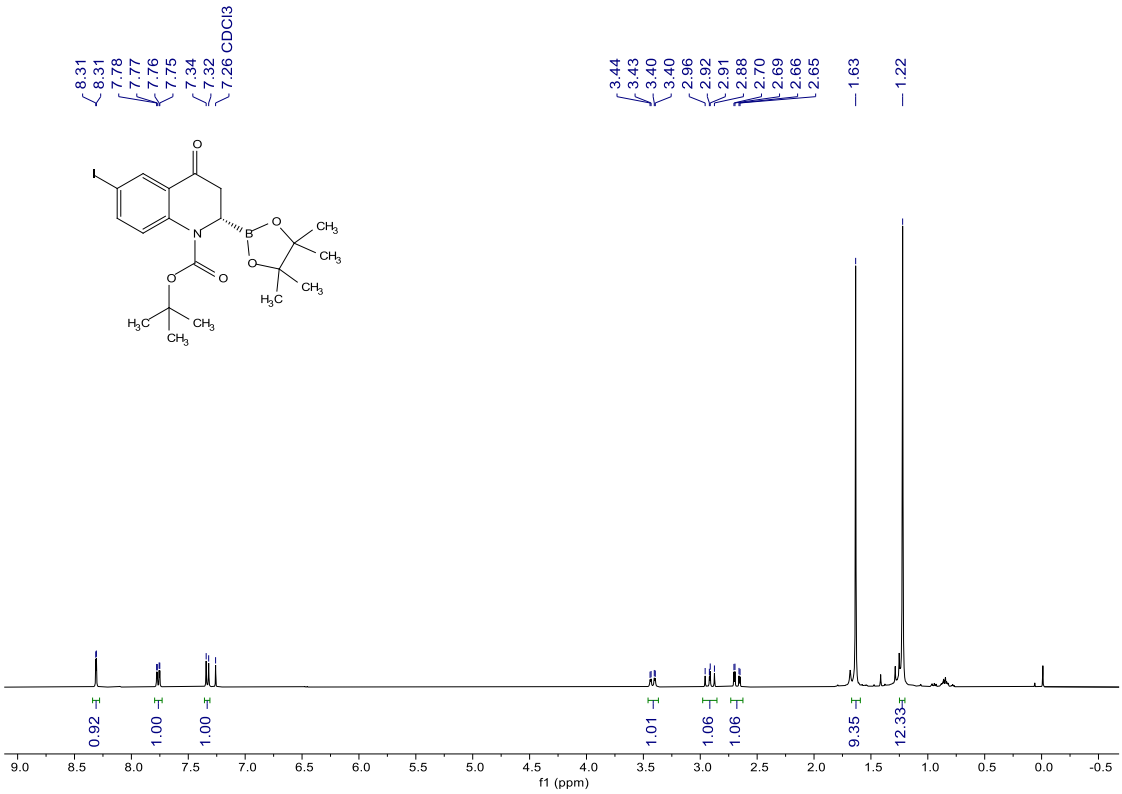


^{11}B NMR (128 MHz, $CDCl_3$)

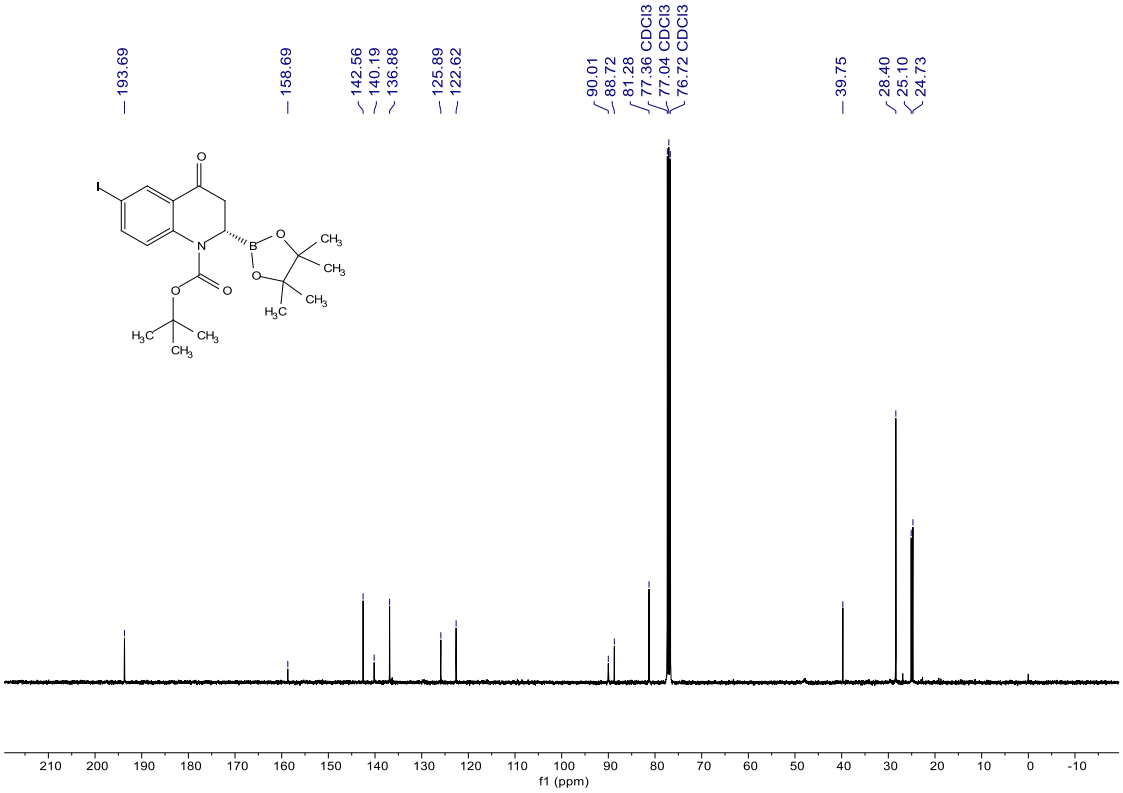


Compound 2r

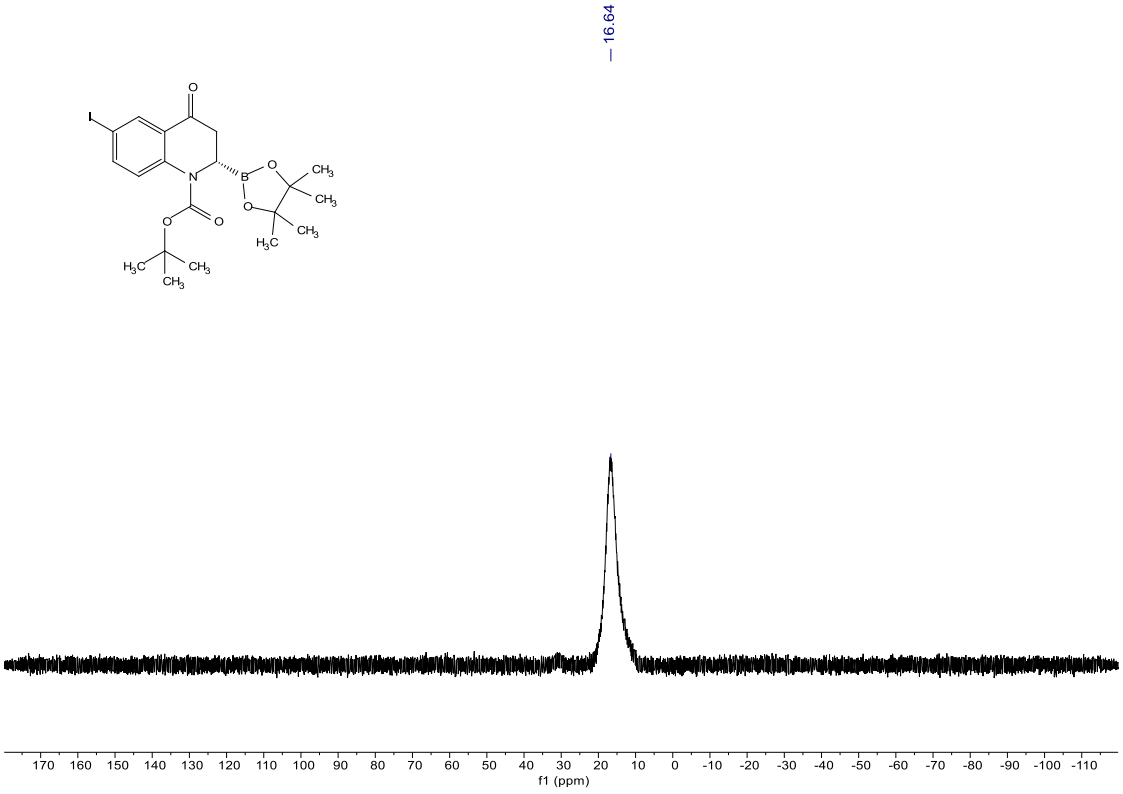
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

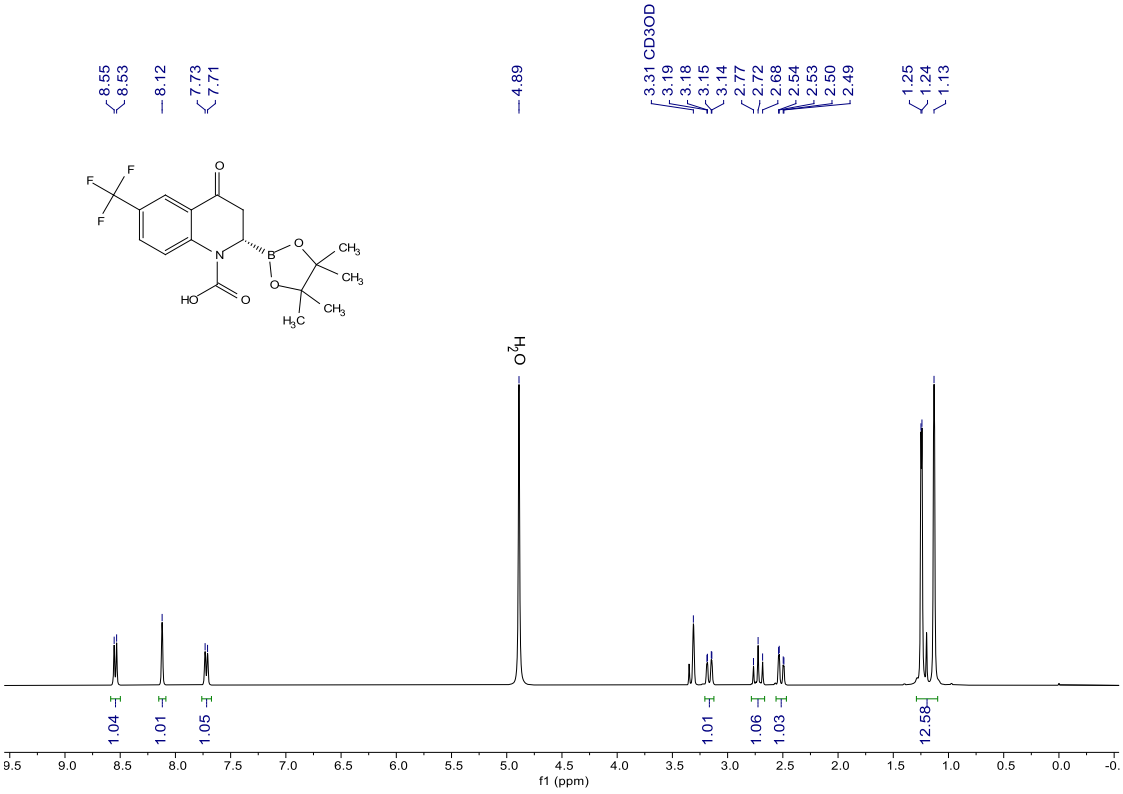


^{11}B NMR (128 MHz, $CDCl_3$)

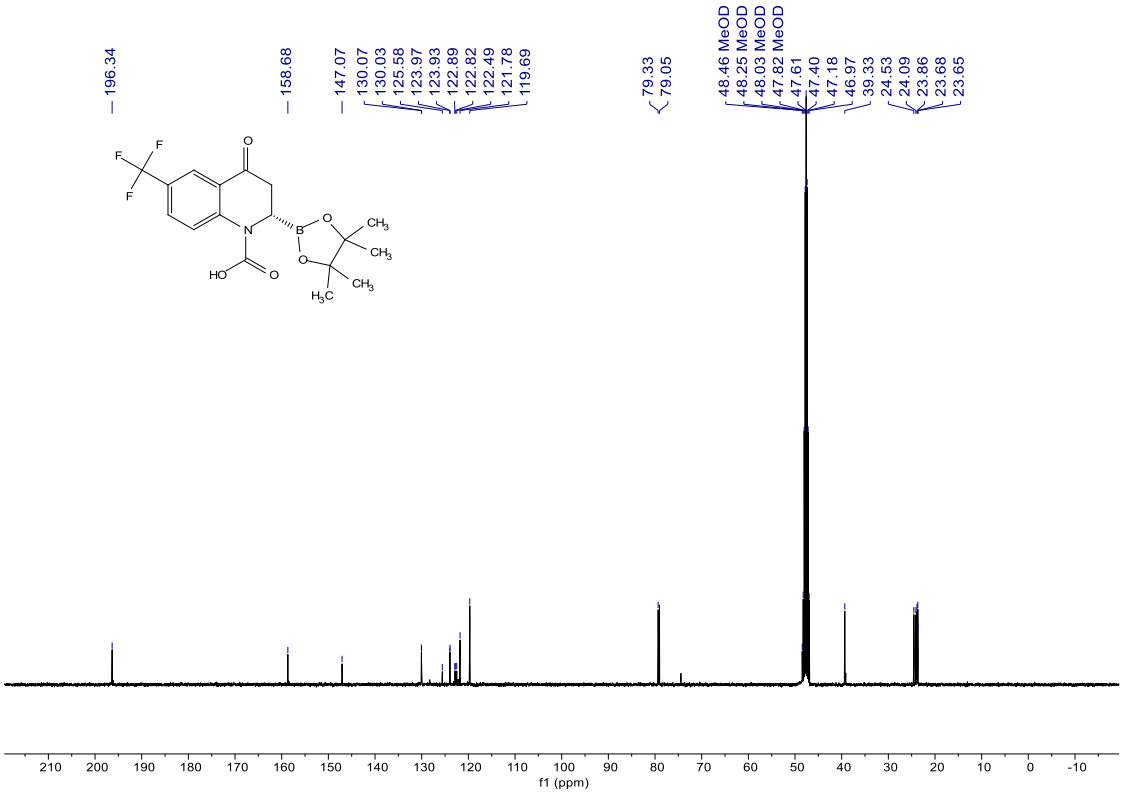


Compound 2s

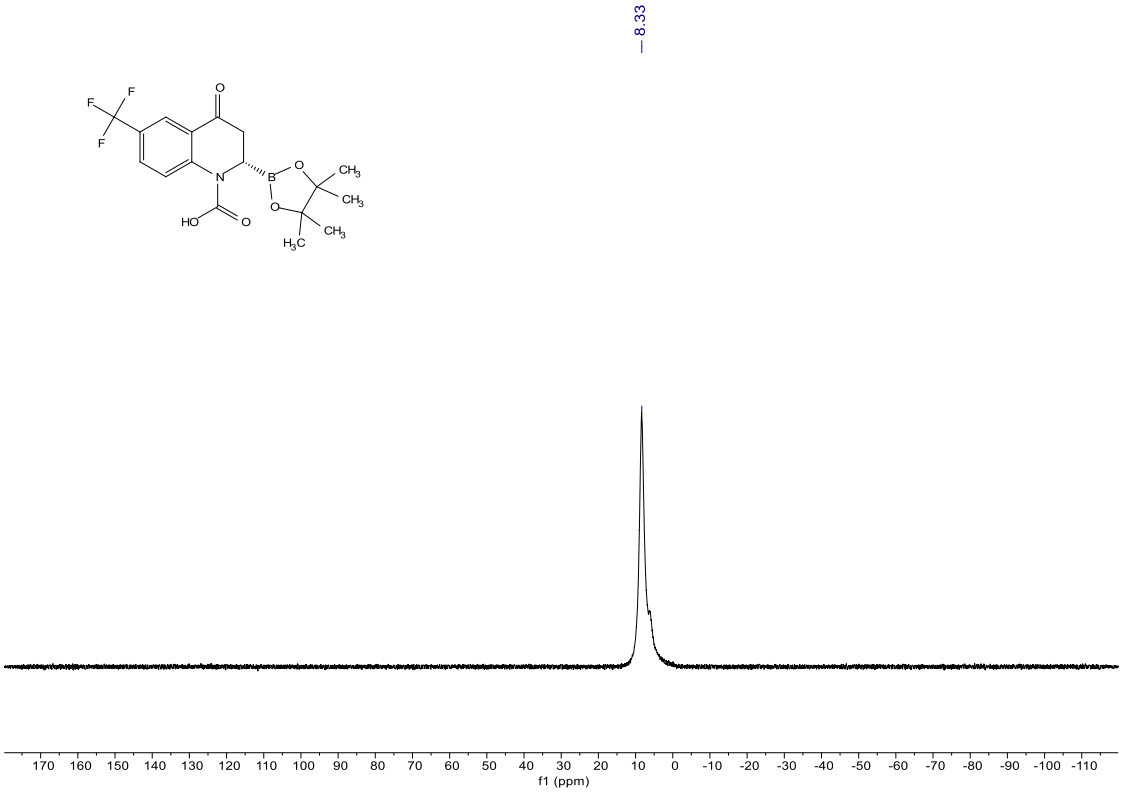
^{1}H NMR (400 MHz, MeOD)



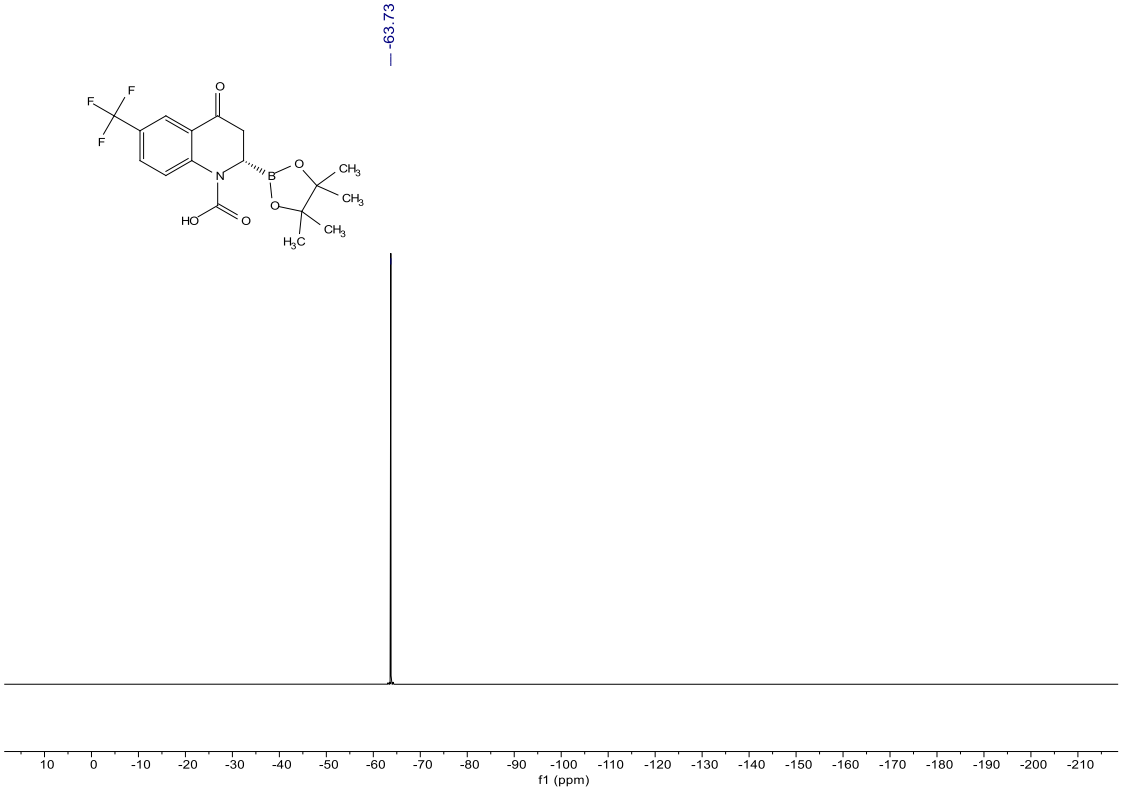
^{13}C NMR (101 MHz, MeOD)



^{11}B NMR (128 MHz, MeOD)

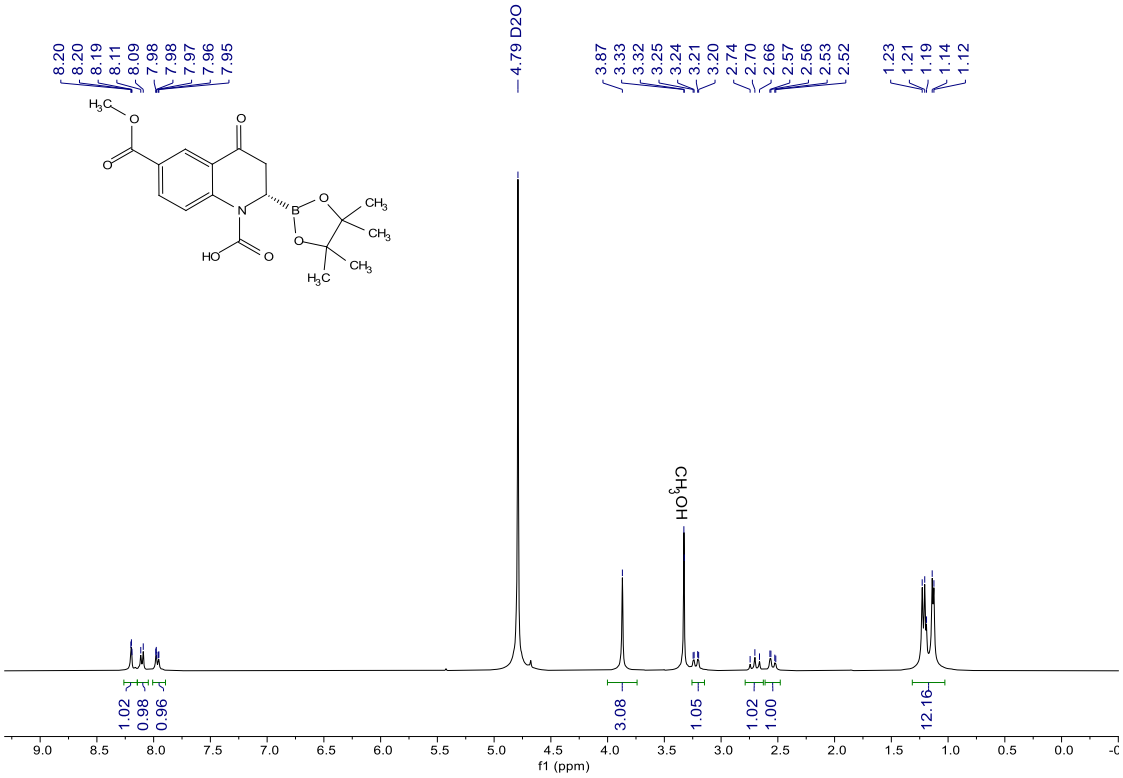


^{19}F NMR (376 MHz, MeOD)

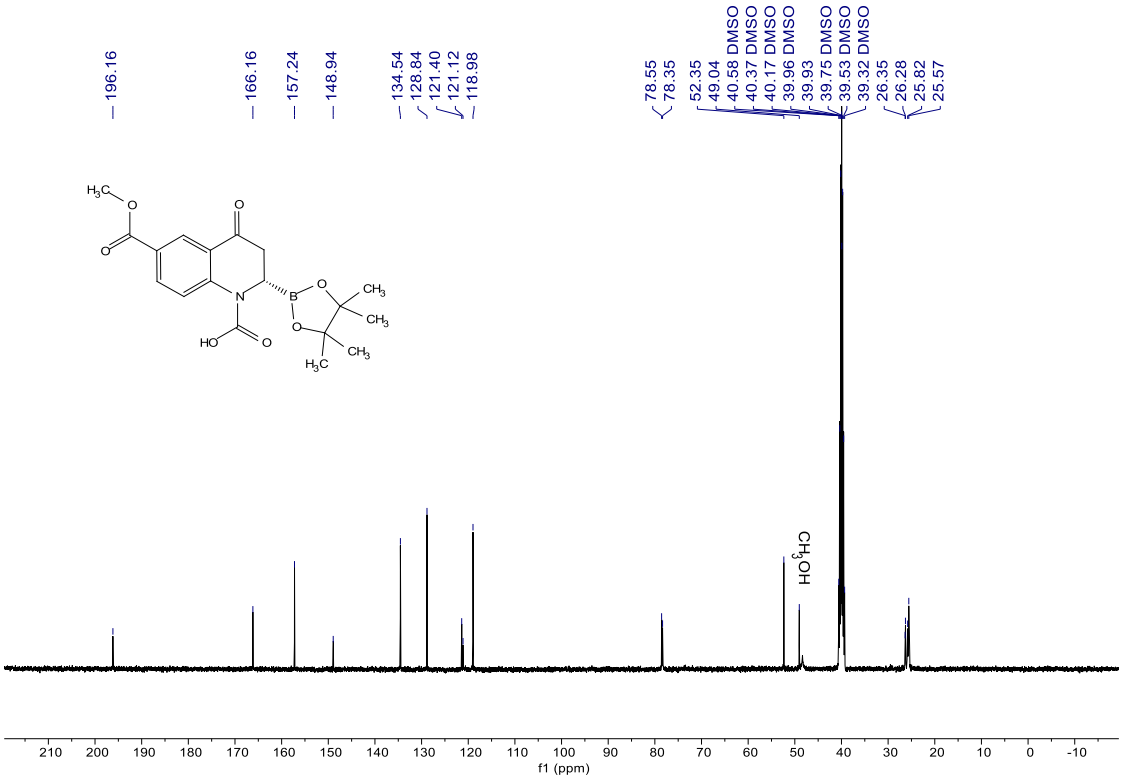


Compound 2t

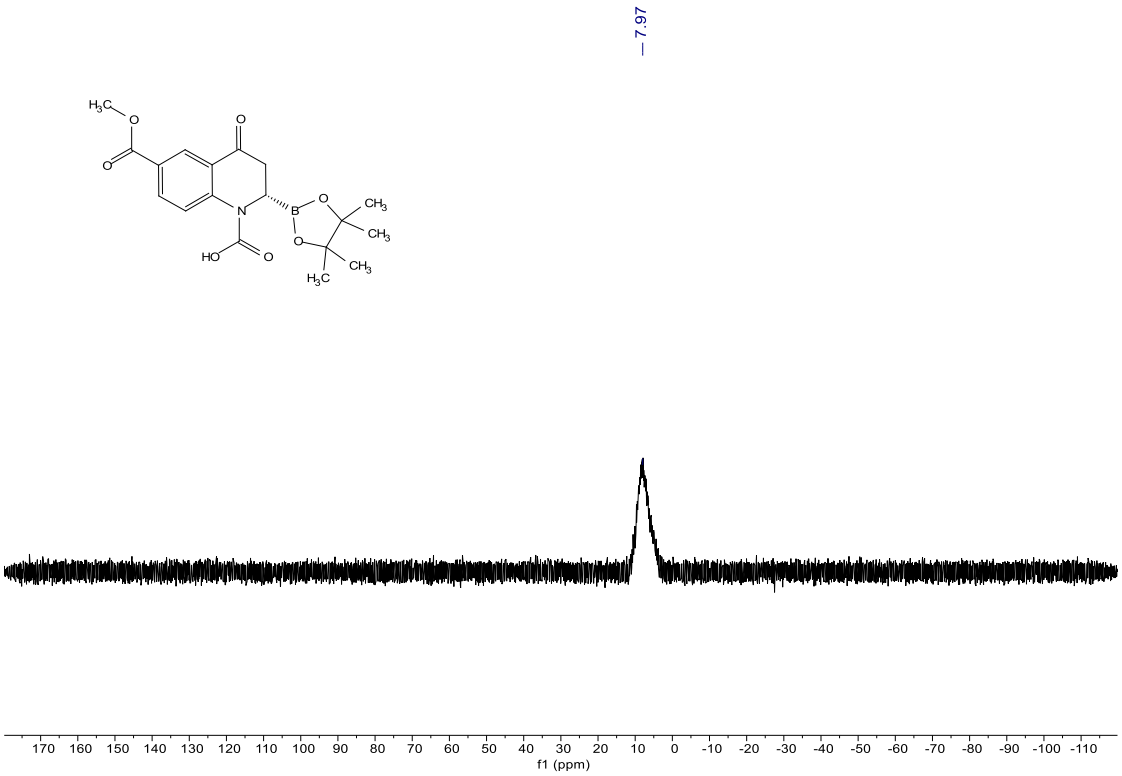
^{1}H NMR (400 MHz, D_2O)



^{13}C NMR (101 MHz, DMSO)

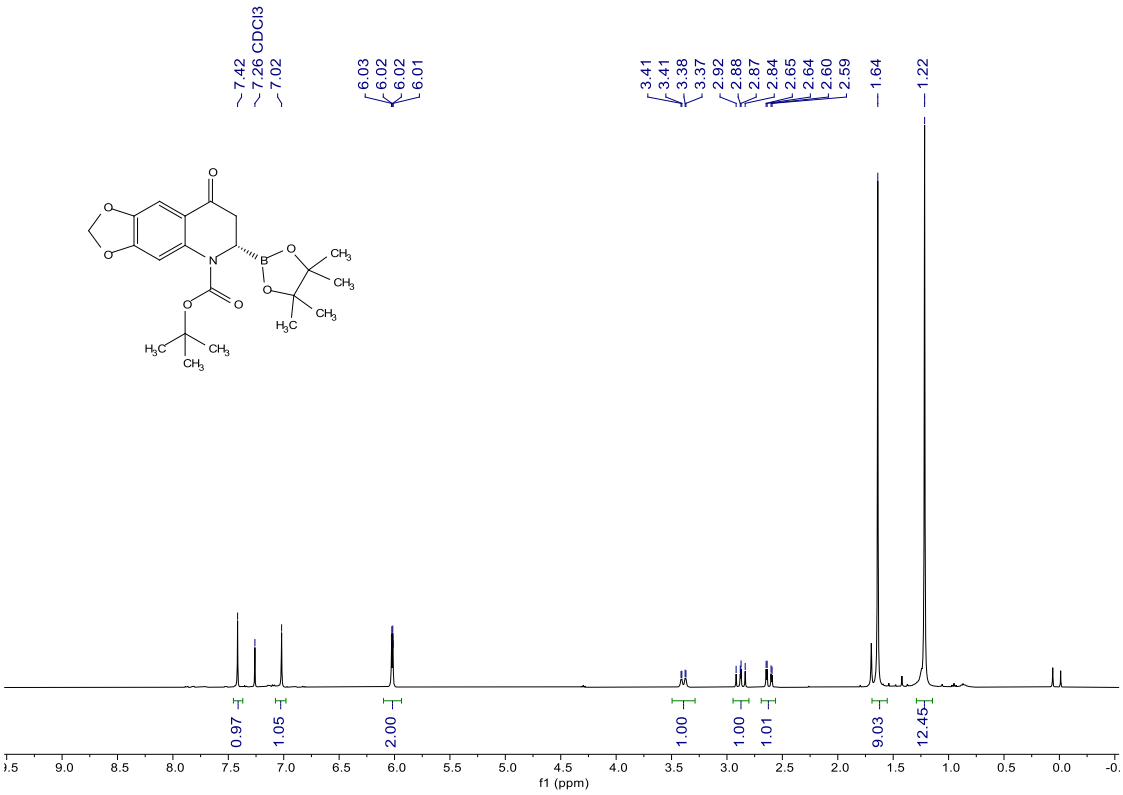


^{11}B NMR (128 MHz, D_2O)

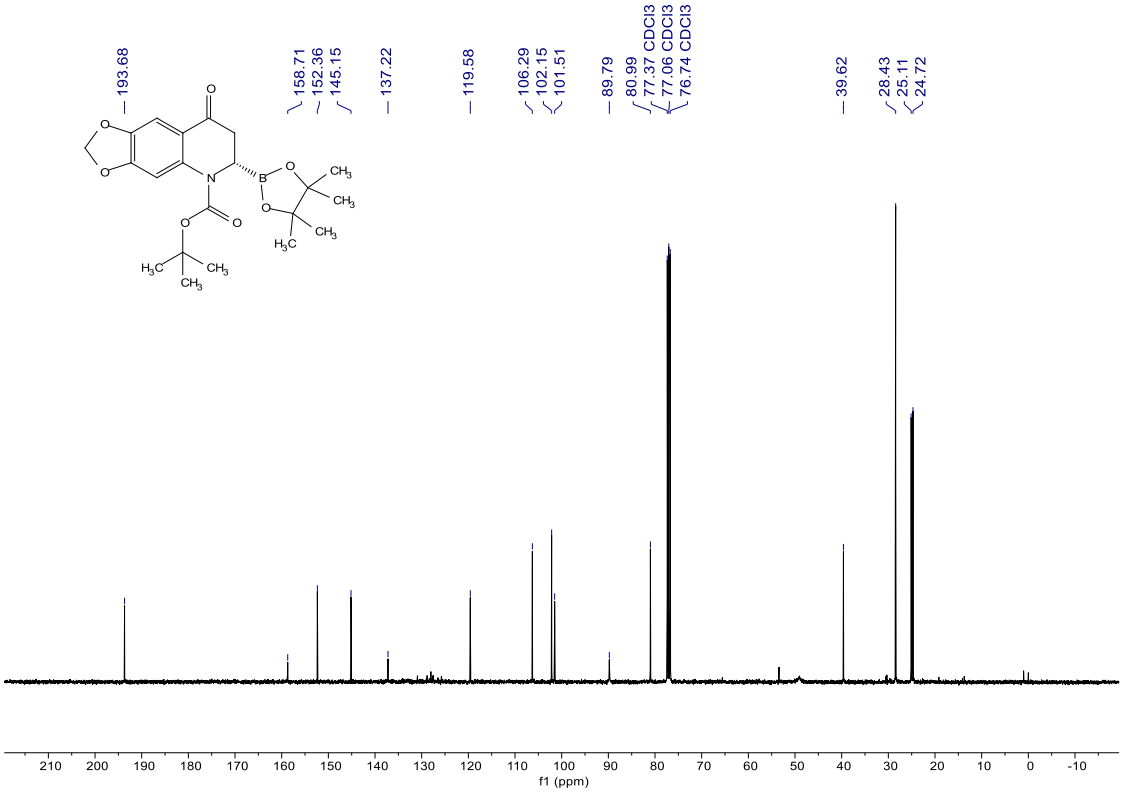


Compound 2u

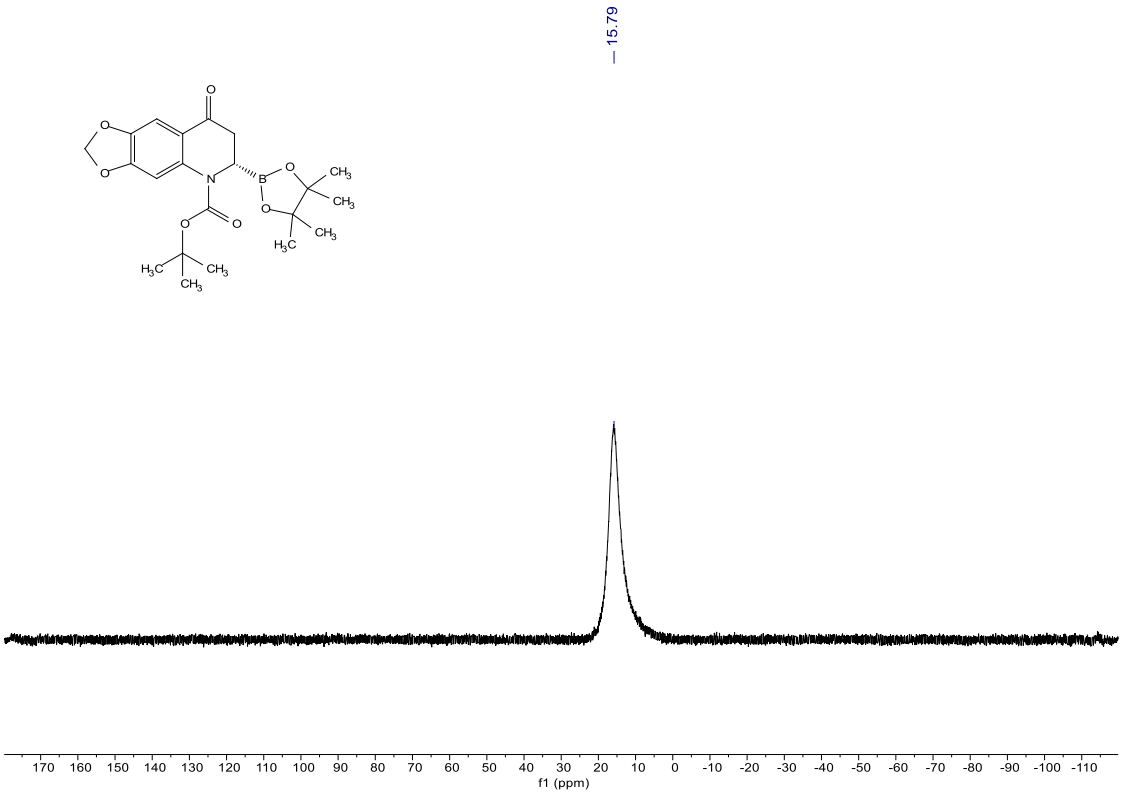
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

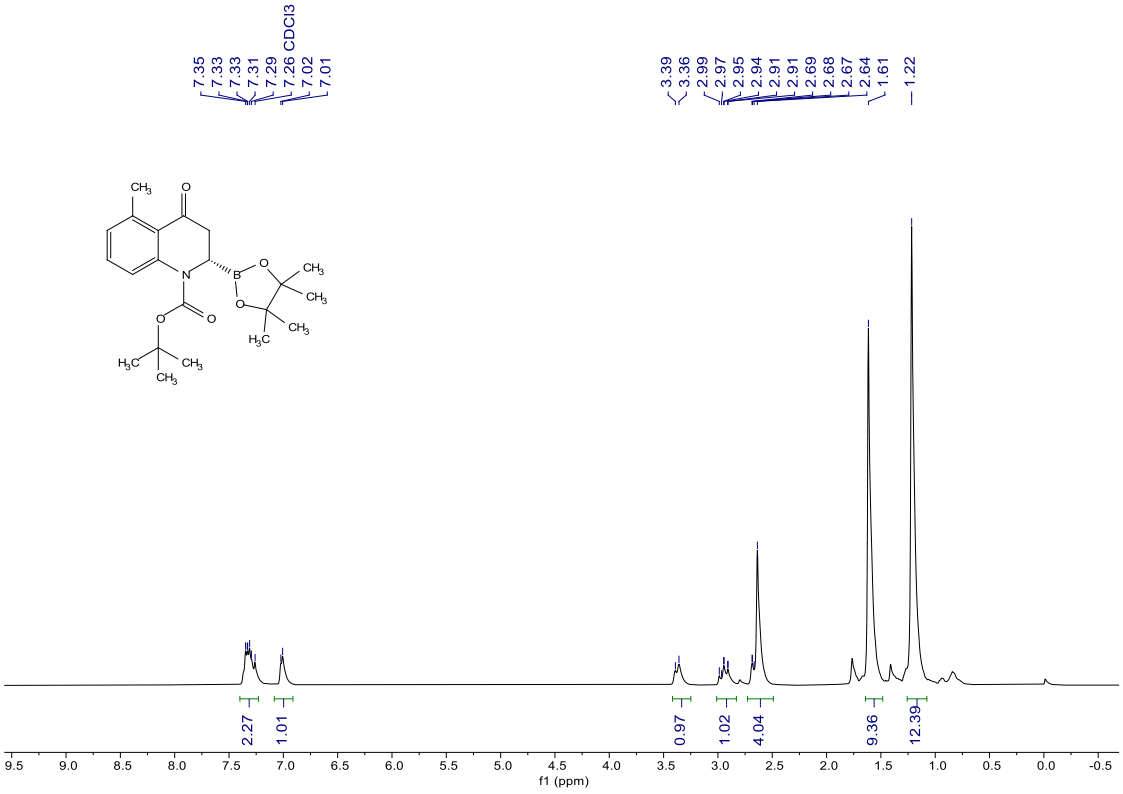


^{11}B NMR (128 MHz, $CDCl_3$)

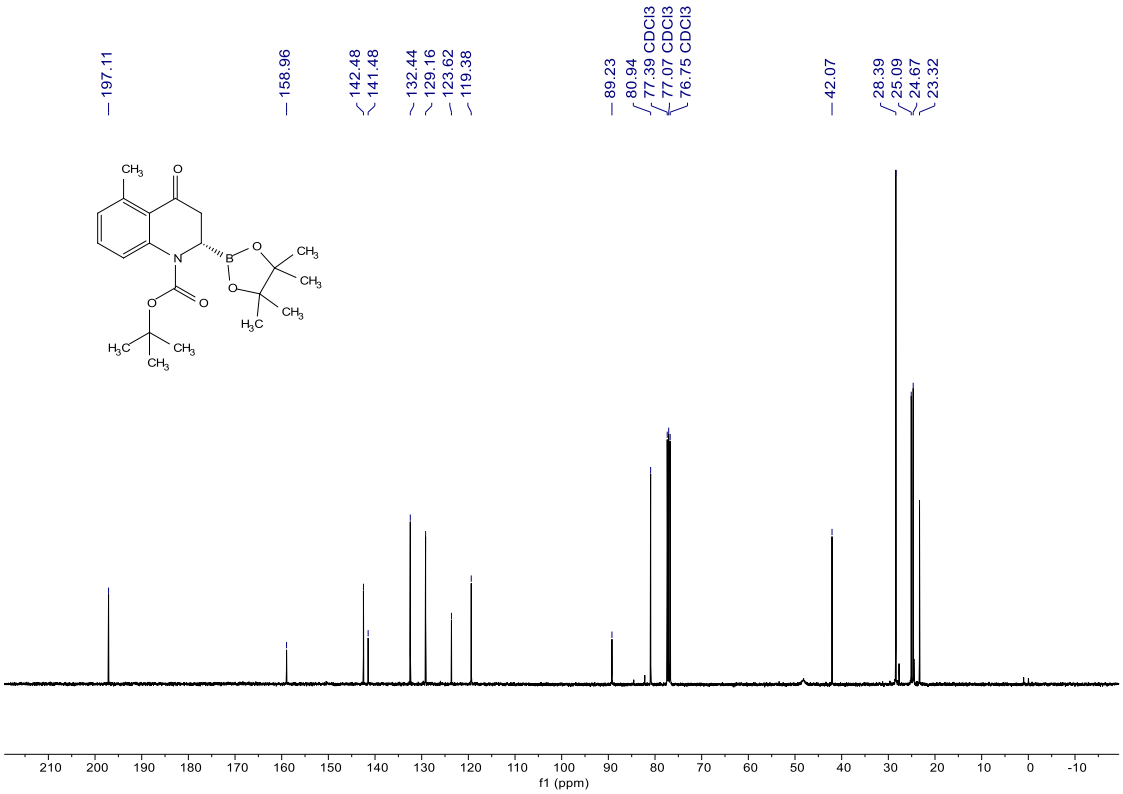


Compound 2v

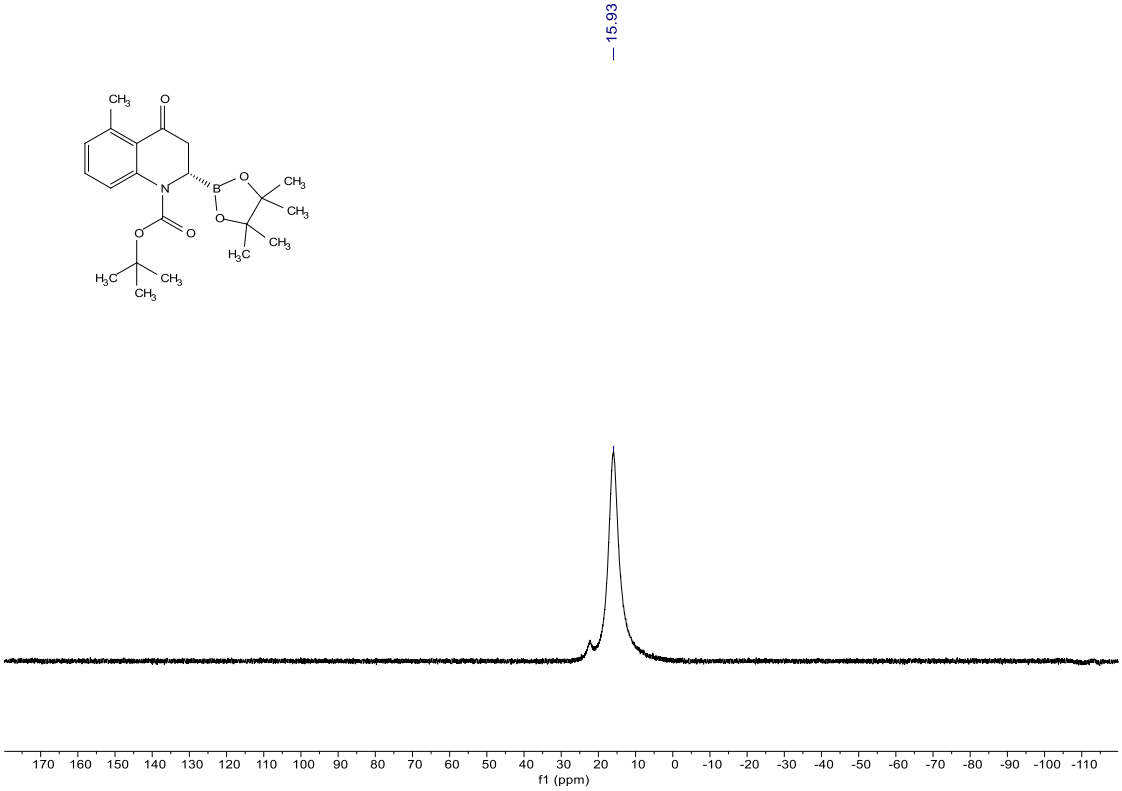
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

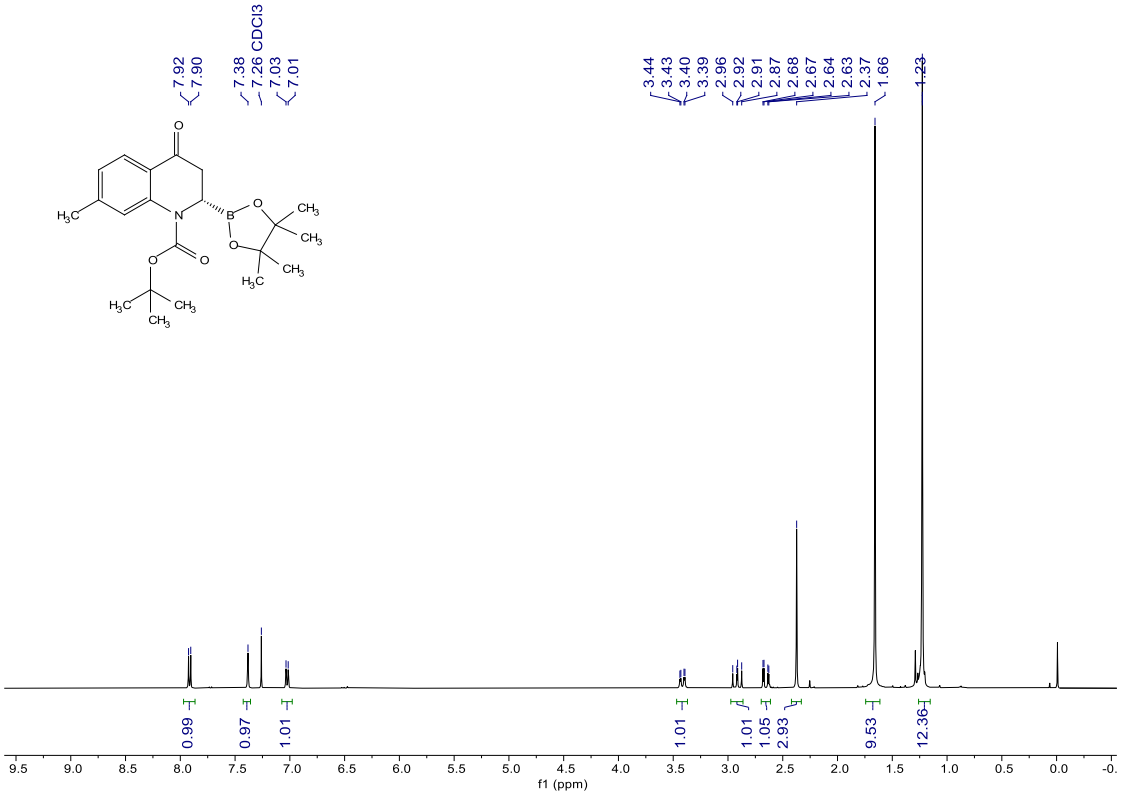


^{11}B NMR (128 MHz, $CDCl_3$)

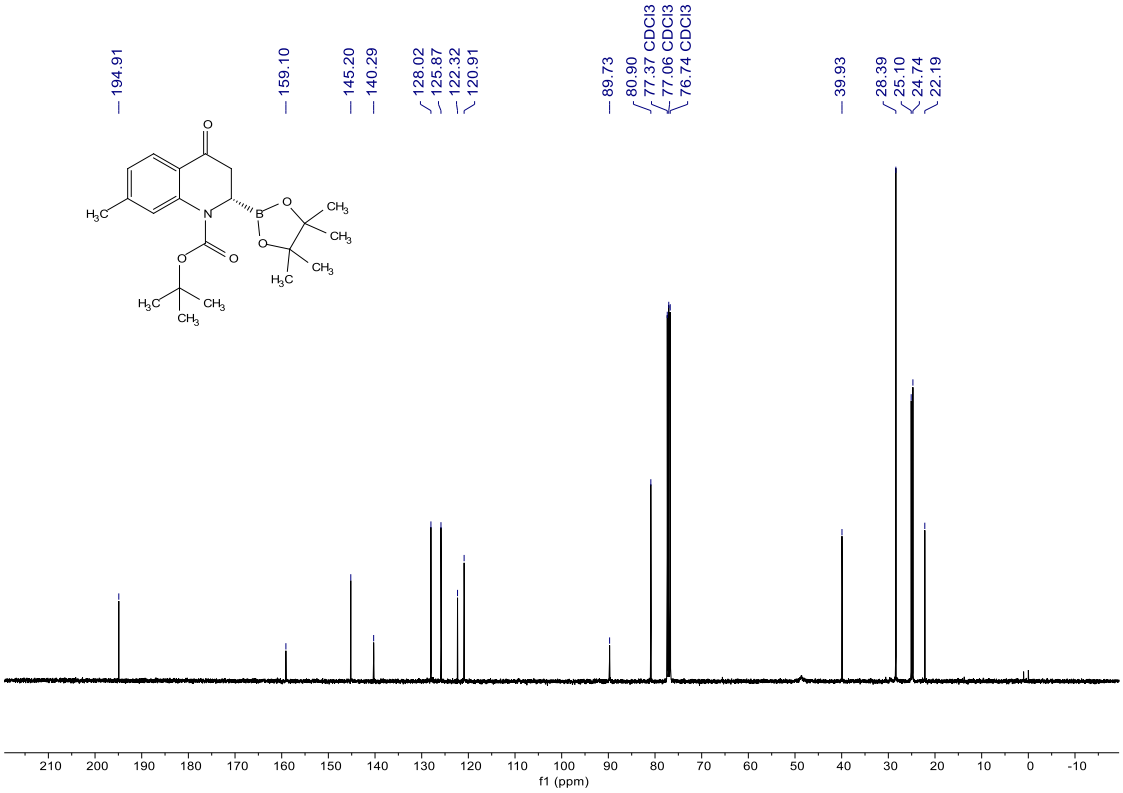


Compound 2w

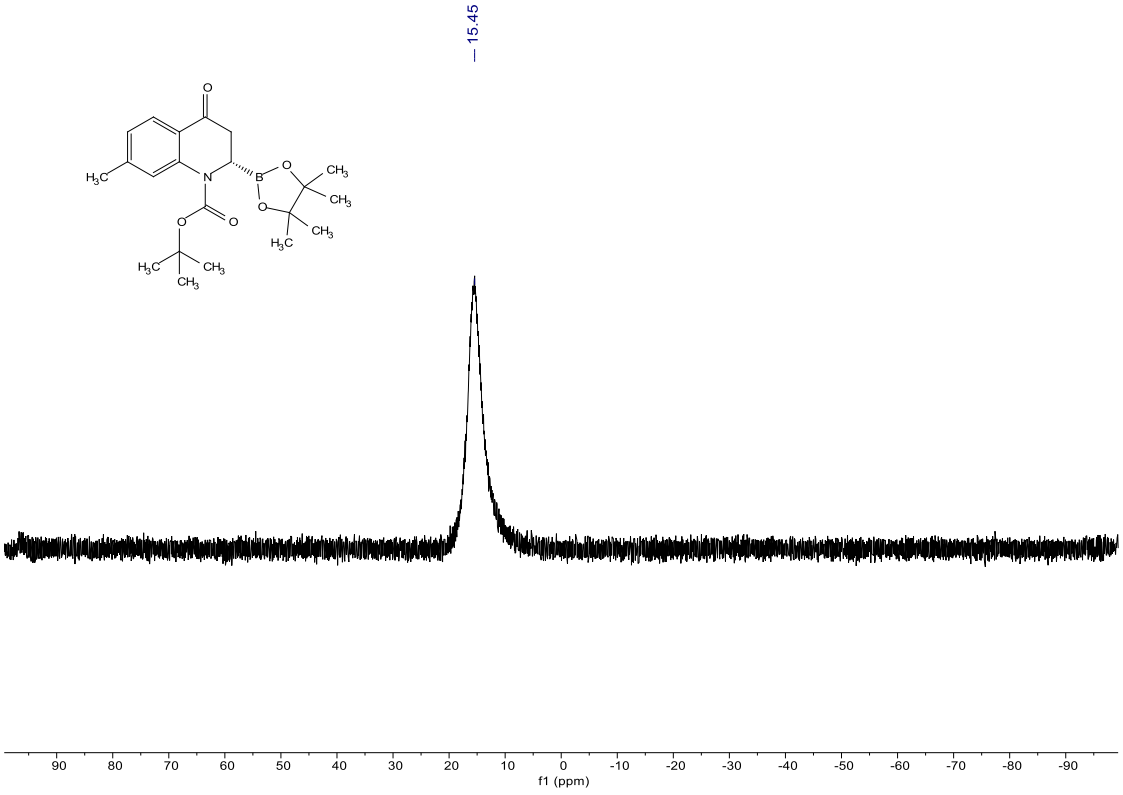
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

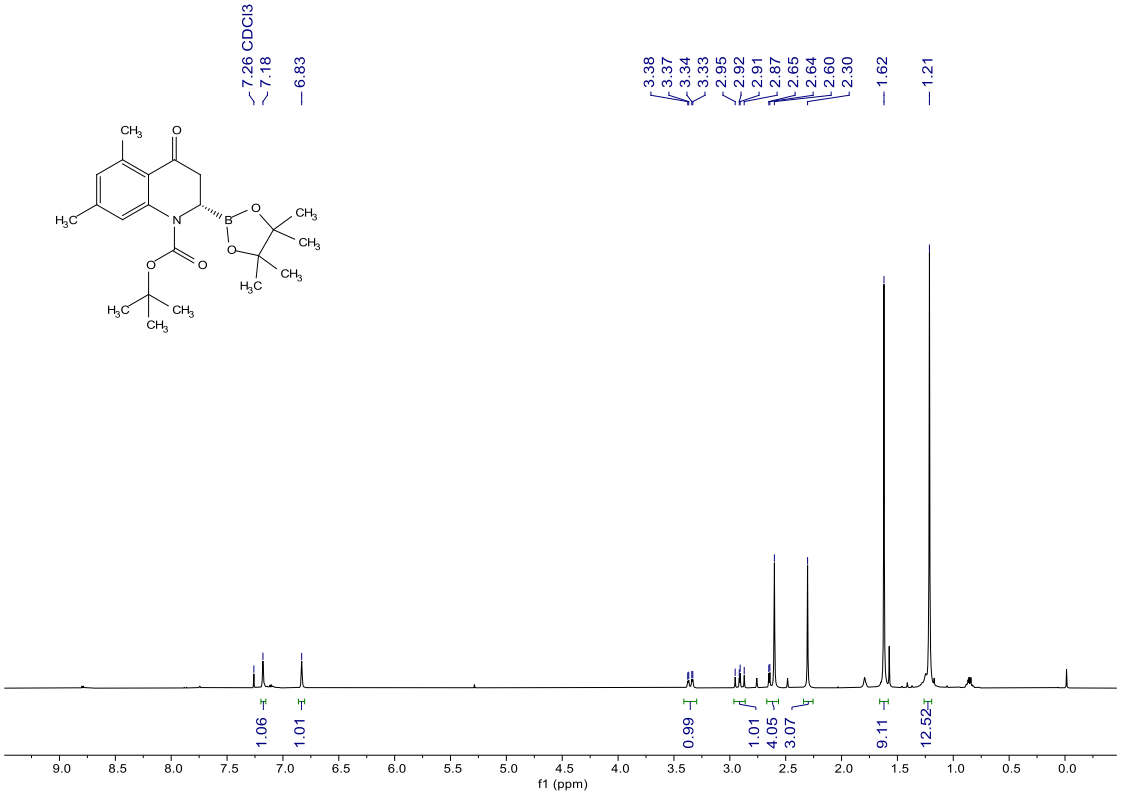


^{11}B NMR (128 MHz, $CDCl_3$)

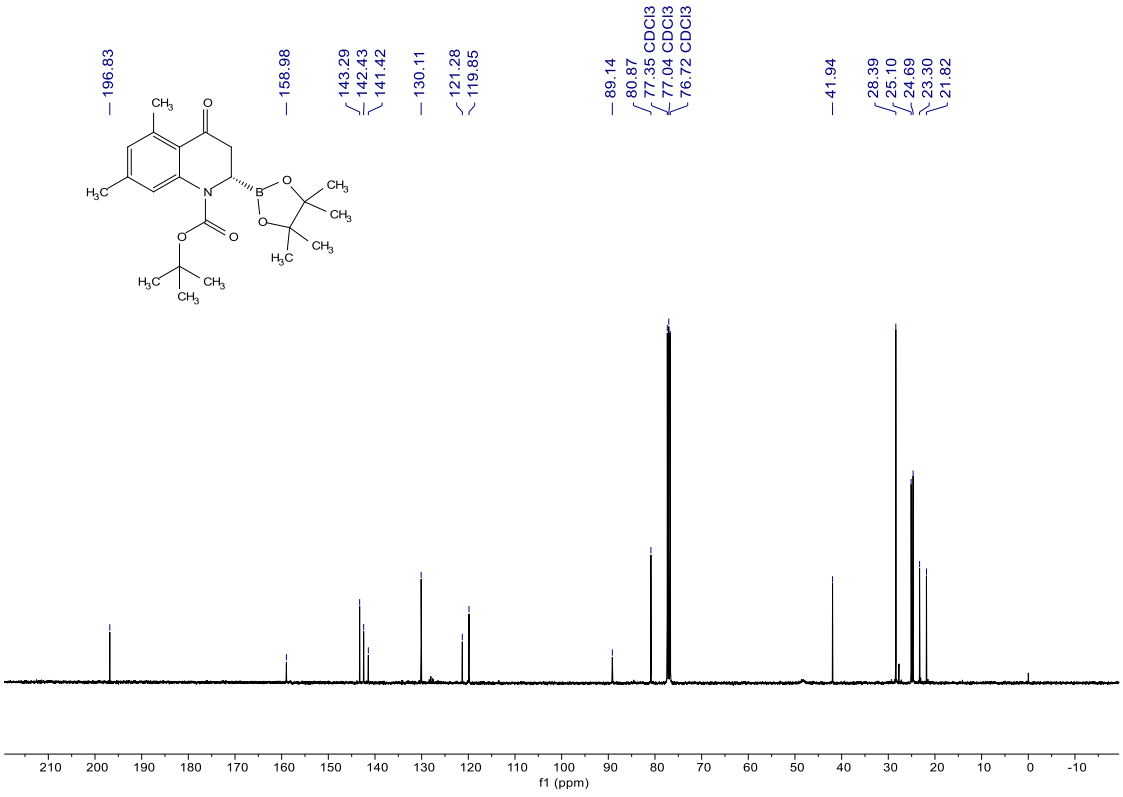


Compound 2x

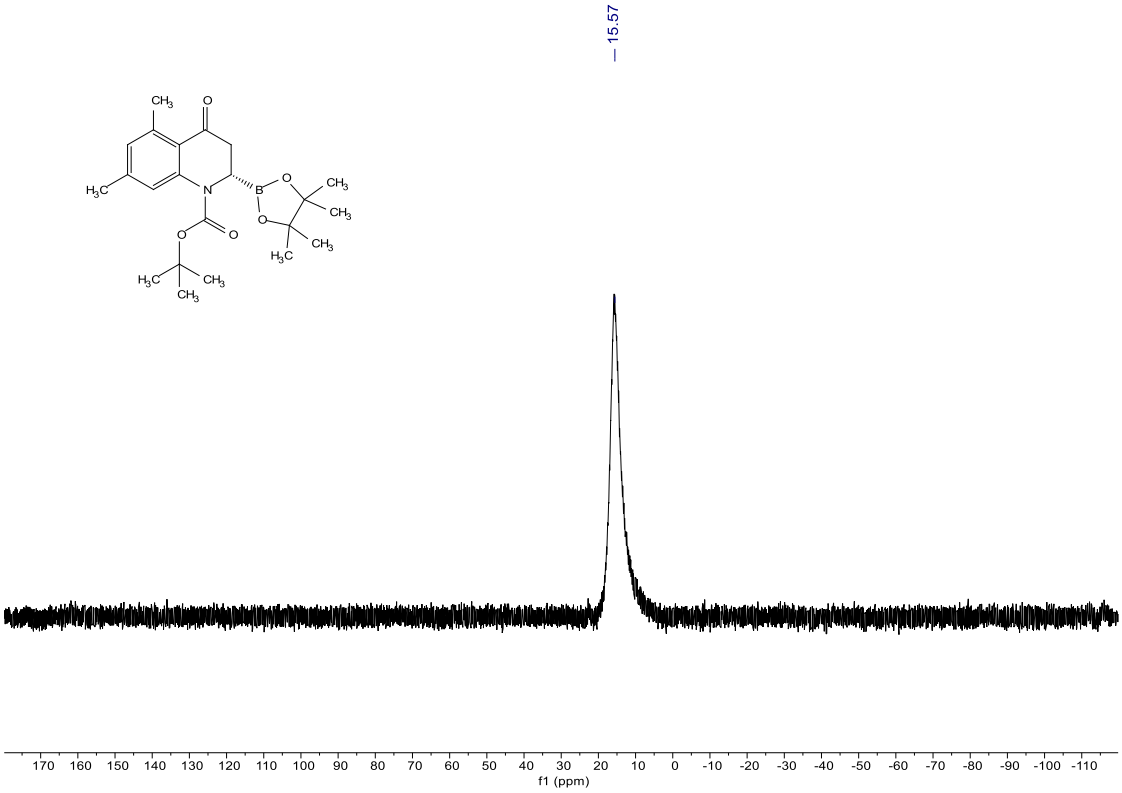
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

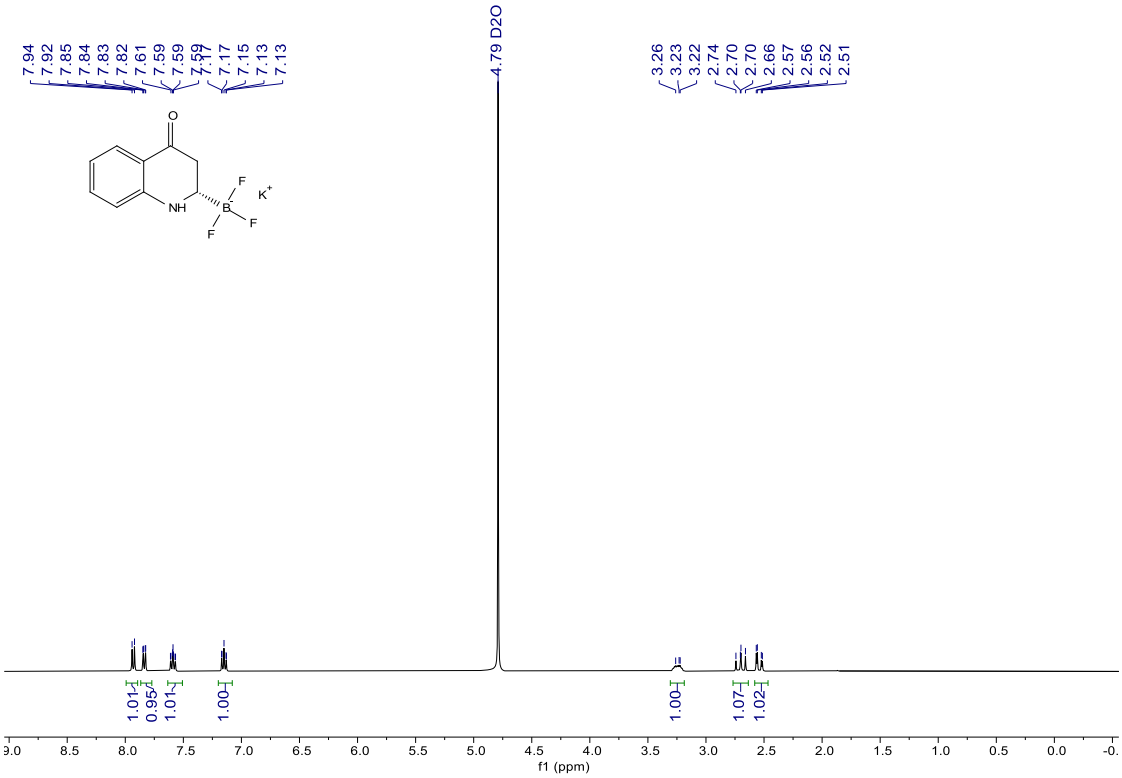


^{11}B NMR (128 MHz, $CDCl_3$)

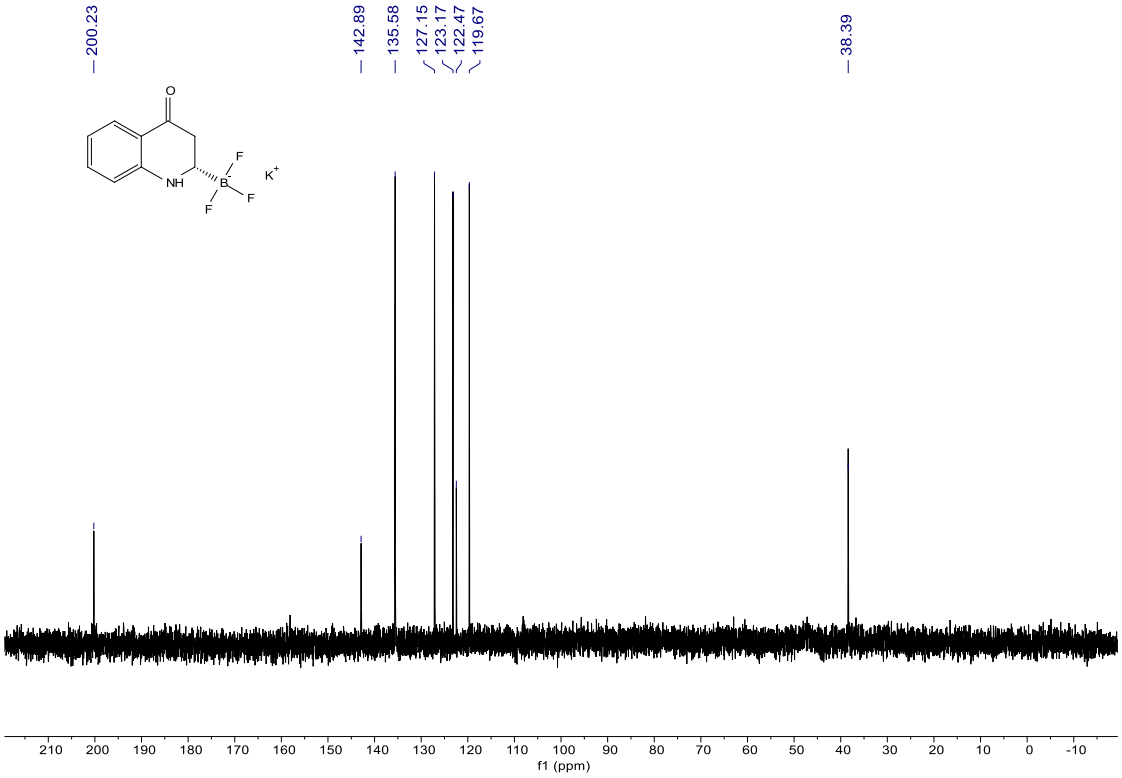


Compound 3a

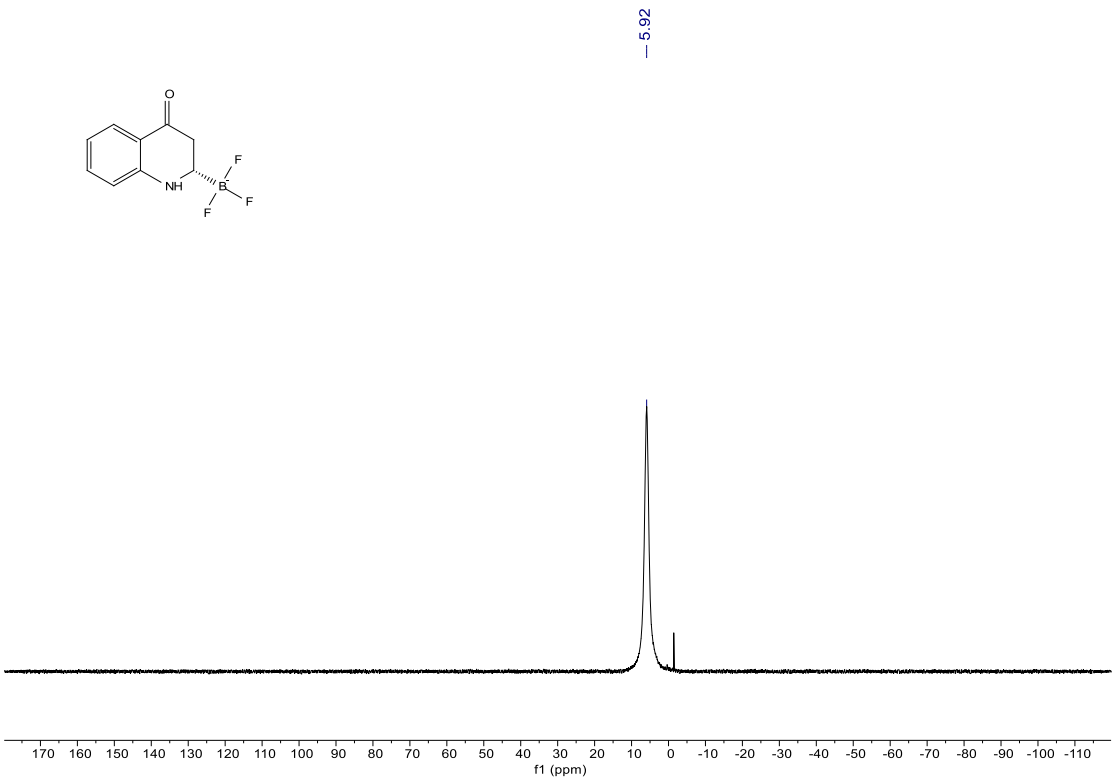
^{1}H NMR (400 MHz, D_2O)



^{13}C NMR (101 MHz, D_2O)

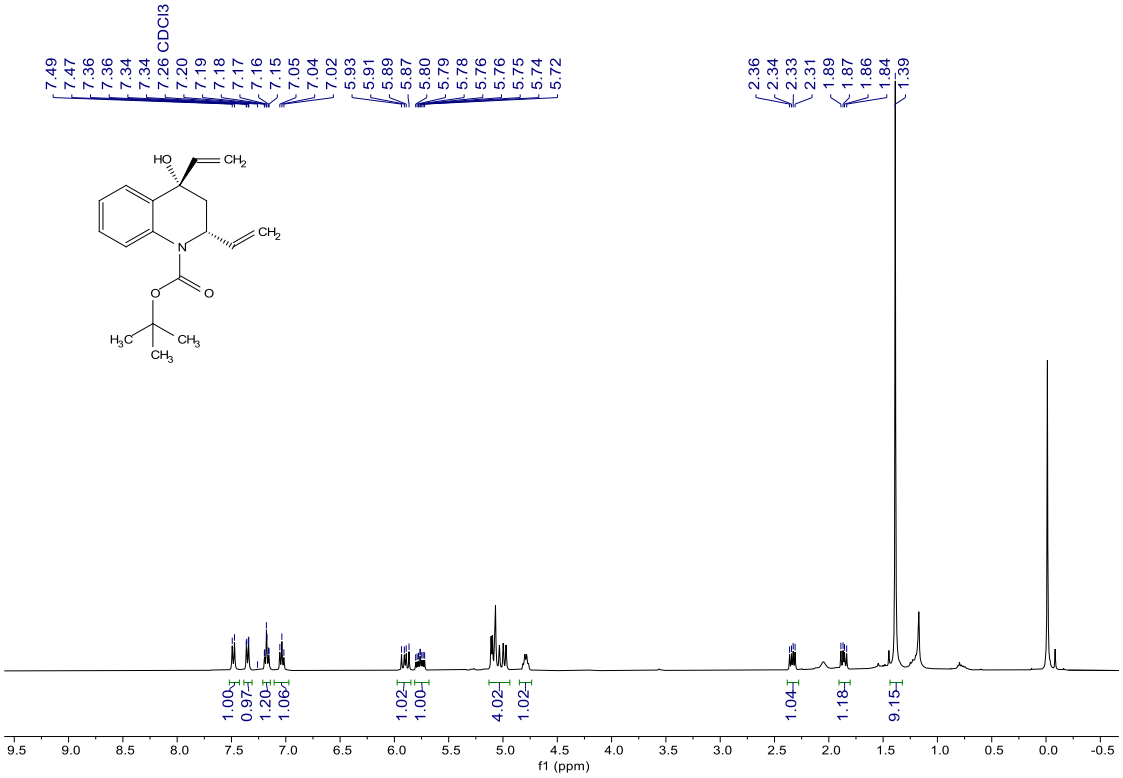


^{11}B NMR (128 MHz, D_2O)



Compound 3b

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)